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ELECTRONIC PROPERTIES AND STRUCTURE OF POLYMERIC ORGANIC SEMICONDUCTORS

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I. INTRODUCTION

Polymers with conjugated bonds occupy a central place in an interesting new class of compounds, that of organic semiconductors, which includes also low-molecular-weight one-component compounds with conjugated bonds (for example, condensed aromatic systems, dyes, etc.), individual charge-transfer complexes, some biological materials such as proteins, and charcoals. The intensive research devoted to these polymers, which were first synthesised as recently as the late 1950's,[1-4] has aroused wide interest in the problem and has created a borderline science: the physics and chemistry of organic semiconductors†. The main attraction of polymers in this context is the fact that their chemical configuration and their structure can be modified as required, thus providing an unlimited number of materials on which to study the nature of the specific properties of organic semiconductors and the modification of these properties in a desired direction.

In recent years, many reviews and monographs have been written on the methods of preparation[24-27] and on the properties[13-17,21,28-37] of semiconducting polymers. It is now recognised that polymers with conjugated bonds, like organic semiconductors of other classes, have a specific type of electronic and atomic structure which gives rise to a combination of properties uncommon in organic compounds: a special electrical and magnetic behaviour, high thermal stability, low solubility, reactivity of a specific kind (in particular, catalytic activity‡), etc. In the present review, which includes all work published up to January

† Progress in the study of organic semiconductors of various classes has been discussed in a number of books and reviews[5-23].

‡ Papers on the catalytic properties of semiconducting polymers, already fairly numerous, will not be considered here because of lack of space. See, for example, Refs. 38–43 and also p.778.

1966 (and a few more recent papers), we shall be primarily concerned with the electrical, magnetic, and structural studies of polymers with conjugated bonds of the classes listed below.

CARBO-CHAIN POLYMERS

A. With Acyclic or Alicyclic Conjugation Chain

1. Polyvinylene ("polyacetylene"), prepared by dehydrochlorination of poly(vinyl chlorides) (PVC),[1,44-55] dehydration of poly(vinyl alcohols) (PVA),[56-62] polymerisation of acetylene[63,64] and polycondensation of acetaldehyde[65,66].

2. Substituted polyvinylenes: poly(phenylacetylene)[2,3,65,67-75] and others[38,39,64-66,76-90].

3. Polyacetylene (poly-yne): $-[C\equiv C]_n-$ or $=[C=C]_n=$.[61,91-93]

4. Poly(cyclopentadiene)[95-97].

B. With Aromatic Rings in the Conjugation Chain

1. Polyphenylene[64,67,71,98-101], polyphenylene-polyvinylenes[102,103], and block copolymers of polyphenylene[98,104,105].

2. "Polybenzenes", polynaphthalenes, and other polyacenes[64,87,97,106,107].

3. Poly(arylenequinones)[67,108-111].

4. Polyarylene-polyacetylenes with triple bonds in the conjugation chain[39,61,91,112-124].

HETERO-CHAIN POLYMERS

1. Containing nitrogen in the conjugated chain: poly(acrylonitrile)§ (PAN)[41,48,78,125-147] and other polynitriles[66,132,148-159], paracyanogen[132], poly(azophenylenes)[67,99,105,160-167,217,392,393], poly(Schiff bases)[132,168-177], polyazines[175,178-180], poly(aryleneamines)[181-185], poly(aminoquinones)[186-188], poly(azoarylenequinones)[189], polytriazines[67,190], polypyridines[191-196], polypyrrole¶[197,198], poly(tetracyanoethylene)[155,199-201], aniline black[172,202,203] and others[49,198,204-210].

2. Containing oxygen in the conjugated chain: polyxanthenes or poly(acenequinone) radicals[48,100,172,208,211-216] and others[16,48,50,124,178,180,217,218].

3. Containing sulphur in the conjugated chain[107,178,180,208,217,219,220].

Various chelate polymers¶ with N, O, and S atoms in the conjugation chain have also been investigated (see, for example, Refs. 221-224).

§ The system of conjugated bonds and the semiconducting properties appear only after heat treatment.

¶ It must be emphasised that these polymers retain their specific electrical and magnetic properties even when the continuous conjugated chain in the molecule is interrupted by bridges of the hetero-atoms or by other groups ($-CH_2-$, $-SO_2-$, biphenylene, etc.): see next column and p. 776.

CHELATE POLYMERS (POLYCOORDINATION COMPOUNDS)

This group includes the poly(phthalocyanines)[225-232], poly(tetracyanoethylenes)[97,200,233-243], polyferrocenes[17,67,208,156,216,244-249], and others[58,67,112,186,221-224,250-268]. These polymers are based on chelate complexes of both transition metals (Cu, Fe, Co, Ni, Mn, etc.) and non-transition metals (Mg, Zn, Cd, Hg).

OTHER TYPES OF SEMICONDUCTING ORGANIC POLYMERS

1. Products of the radiation-thermal treatment of polyethylene[269-279] and poly(acrylonitrile)[131,280].

2. Compositions including polymers and metallic powders[231,281-288].

3. Complexes formed by various polymers with halogens[74,174,185,197,198,205,211,289-294] and with other organic substances[51,295,296], with organic molecules[185,290,295,297,298], and also with O_2.[74,195,198,275]

II. SPECIFIC PROPERTIES OF SEMICONDUCTING POLYMERS

1. Chemical Structure of the Molecule and Structure of the Material

The electronic properties of solid organic compounds able to crystallise only in the form of molecular lattices are determined, on the one hand, by the properties of the separate molecules and, on the other hand, by the way in which these molecules are packed and by their mutual interactions, i.e. by the parameters of the solid as a whole. It is best to consider these two factors separately.

From the point of view of the chemical structure of the molecule, the principal feature common to all semiconducting polymers is a system of conjugated π-bonds. The properties of such a system reveal themselves: (1) in the colour of the material, which becomes deeper as the degree of conjugation in the molecule increases (and can become black, for example after heating to 400°)[3,45,59,64,72,121,122,177,299] and less intense when the conjugation is perturbed[45,122,123,125,180]; (2) in the infrared spectra (appearance of new characteristic bands[49,59,60,83,91,93,129,239,299,301] and sharp increase in background absorption[98,239,248,302,303]); (3) in the u.v. spectra (development of strong characteristic absorption[133,134,167,242]) and in the fluorescence spectra[69,304-306]; (5) in the electrical properties (see Section II, 2).

However, recent work has shown that the earlier views, according to which the molecule of a semiconducting polymer can be visualised as a one-dimensional crystal with an uninterrupted system of conjugated π-bonds[30,307], are incorrect. There is abundant evidence for this statement. The usual sequence of colour changes of polymers subjected to heating and irradiation (yellow to brown) is not what we would expect from a gradual increase in length of the conjugated system (yellow, red, purple, blue)[52]. Heating of the polymers does not give rise to a clear long-wave shift of the absorption maximum in the u.v. spectra, but only increases the intensity near the long-wave edge of the band[133,134,242]. Heat-treated poly(methyl vinyl ketone)[300], unlike PAN[299], does not show a long-wave shift in the infrared spectrum. The electrical properties are not seriously

impaired[81,122,124,164,165,175,176,178,180,184] when the conjugation in a polymeric chain is destroyed by introducing bridging groups such as CH_2, O, N, and the biphenylene grouping, whose rings have been shown by NMR not to be coplanar[99]. Finally, it is clear from the fluorescence spectra that an increase in molecular weight is not accompanied by an increase in the length of the conjugated system[69], and the ESR spectra, which sometimes show a hyperfine structure for solutions[49,185], indicate that the unpaired electron is delocalised only over 2–7 monomer units[56,68,74,123].

It follows that the continuous conjugated chain in semiconducting synthetic polymers is usually of limited length (probably only a few monomer units). Whatever the cause of this phenomenon† we must conclude that the minimum length of uninterrupted conjugated system of π-bonds needed to give rise to the specific electronic properties of the polymers is no greater than the size of the conjugated systems in low-molecular-weight one-component compounds and in individual charge-transfer complexes. This conclusion is an argument for the general similarity of the electronic nature of all organic semiconductors.

Before proceeding to a discussion of the solid-state structure of semiconducting polymers, we must stress the fact that this structure is composed of oligomeric molecules. Thus, most workers have been unable to obtain a molecular weight higher than 3000, or a degree of polymerisation in excess of 10.[2,83,120,122,160,185,194,195,308,309] According to Berlin[15,160,309], this "oligomericity" is due to a gradual deactivation of the radicals with increasing length of conjugated chain, arising from the increasing delocalisasation of the unpaired electron. However, not all polymerisation processes involve radicals [for example, the dehydration of poly(vinyl alcohol), the dehydrochlorination of poly(vinyl chloride), "onium" polymerisation], and we can therefore envisage gradual deactivation of any reaction centre — not just free radicals — or focus attention on the decrease of the solubility of the product with increasing degree of polymerisation[308], particularly since polymers with conjugated bonds are prone to association in solution (anomalous viscosity).

Because of their low molecular weight, semiconducting polymers can exist not only in the amorphous state but also as crystals with a molecular lattice‡[61,122,135]. Intermolecular interactions in this type of lattice are fairly weak on the whole, as shown by the poor electrical conductivity of the crystalline polymers and also by the instability of the lattice towards heating: the oligomer usually becomes amorphous even at 200–300°,[57,59,60,122,181,310] although some increase in crystallinity can be observed in the initial stages (below 200°)[57,59,310,311].

However, stable local formations exist within the weak lattice, as evidenced by the ESR signal in solution[3,49,68,83,105,195,306,312], from which we can deduce that the concentration of unpaired spins has not changed[3,68,195], by the anomalous viscosity at high dilutions[135,160-162,184,190,195,313], and by the identity of the electronic spectra in the solid state and in solution, all of which have been observed for charge-transfer complexes based on polymers[293]. The nature of these stable formations is discussed tentatively in Section III.

The ease with which the molecular lattice of polymers collapses on heating is due not only to the instability of lattices of this type but also to the fact that a specific amorphous structure is produced[47,59,61,98,122,175,181] in which interaction between π-electron systems and the polar groups of oligomeric molecules can readily occur. This is apparent both from the observed chemical processes[59,60,129,133,134,146,170,299,300] and from the electrical and magnetic properties discussed in Section II, 2 and II, 3. The overall conclusion from the available data is that the specific structure of semiconducting polymers is due to regions with a relatively large number of conjugated bonds (usually, systems of condensed aromatic rings) separated by disordered regions in which the conjugation is weak[47,85,122,128,135,145,191,200,227,237,242,269,270,275] (see p. 780).

Heating to high temperatures (upwards of 500–600°) produces a gradual increase in the size of the conjugated regions and slowly raises the degree of order of the structure[47,59,123,144,146,147,275,314,315], i.e. it makes the properties of the polymers closer to those of charcoals. Of course, crosslinking processes and the formation of a three-dimensional structure can be rather slow[78,120,316]. In particular, a correlation has been found[61,91-93,314,317] between the structure of the pyrolysis products and the structure of the monomer unit in the starting molecules, and it has been shown that carbons can be obtained with a chain (poly-yne or cumulene) rather than a floor-block structure.

It will be clear from the subsequent discussion that, in order to understand the general features of the behaviour of semiconducting polymers, we need to make allowance for the interplay of the two factors considered here: the chemistructure of the molecule and the structural ordering of the material[124,165,175].

2. Electrical Properties

The electrical characteristics of polymers with conjugated bonds can vary widely: from those of dielectrics (as in the case of low-molecular-weight organic semiconductors and weak charge-transfer complexes) to those of semimetals (as in the case of strong charge-transfer complexes and carbons). Values of the electrical conductivity σ vary from 10^{-15} to $10^{2}\ \Omega^{-1}\ cm^{-1}$; the activation energy for conduction E_σ varies from 2 to 0.01 eV§. The variation of σ with reciprocal temperature is typically that expected for a semiconductor: the electrical conductivity increases exponentially with temperature T according to the law

$$\sigma = \sigma_0 e^{E_\sigma / kT}.$$

The absence of polarisation effects during the passage of current is evidence that the conductivity is electronic rather than ionic[57,58,111,172,198,201,214,272,295]¶. The electrical properties are strongly influenced by the adsorption of oxygen[78,85,122,127,135,176,198,229,247,248,259,290]† and other substances[48,51,57,181,197,198,205,225,259,270], and also by

† In all probability, it is due partly to the low degree of polymerisation characteristic of polymers with conjugated bonds (see below) and partly to spontaneous disturbances occurring during the synthesis of the conjugated system.

‡ Some observations suggesting a correlation between the degree of crystallinity and the structure of the molecule have been reported[61,122,165,175]. It is interesting to note also that some degree of preferential orientation of the macromolecules can be induced in weakly crystalline polymers by pressure or by stretching[57,128,130].

§ For a number of polymers, semimetal characteristics have been reported[132,172] ($E_\sigma \leq 0$).

¶ Some workers discuss the possibility of ionic conduction[54,111,129,201,272,312], although polarisation effects do not necessarily imply an ionic mechanism[111].

† However, oxygen effects are often absent[57,68,154,178,179,181].

pressure [177,215,294,318], illumination (see p. 777), and irradiation [131,272,319]. When the resistance is not too high, surface conduction does not appear to distort the results [57,135,217]. But some workers point out that measurements with d.c. do not give a sufficiently complete picture of the electronic properties of polymers [200,237]. Nevertheless, the main conclusions derived from measurements with a.c. [144,200,201,233,237,238,243,268,269,271,277] and with d.c. (see Section IV) are identical, and the results obtained by d.c. and a.c. measurements of the conductivity of poly(phthalocyanines) [230] are indistinguishable: we can therefore accept the d.c. method (which has been used in the vast majority of investigations of organic semiconductors) as entirely correct. Since the exact mechanisms of electrical conduction are not yet fully understood (see Sections IV and V), we cannot unequivocally ascribe the breaks often observed in the linear plots of $\log\sigma$ against $1/T$ to transition from impurity conduction to intrinsic conduction, particularly since Pohl's calculations for poly(acenequinone) radicals [172,214] would appear to exclude the possibility of impurity conduction by extraneous contamination. In general, with systems as inhomogeneous as polydisperse conjugated polymers it is hardly meaningful to talk of intrinsic conduction, and the term "impurity conduction" [145,277] can only refer to the presence in these polymers (excluding high-temperature polymers) of molecules or regions with a degree of conjugation sufficient to ensure appreciable ionisation at ordinary temperatures, the fraction of the total mass involved being small. Ohm's law has often been found to hold up to 10^3–10^4 V cm^{-1} in studies of semiconducting polymers [169,179,201], although departures are occasionally reported [64,214] at quite small fields of the order of 10–100 V cm^{-1}.

The sign of the current carriers (from measurements of thermo-e.m.f.) can be either positive or negative. However, oxygen always affects the thermo-e.m.f. in the positive direction [127,135,136,154,229,269], and it is at least possible that the current carriers, in contrast to the early views on organic semiconductors [5], consist largely of electrons (as indicated by most of the measurements in a vacuum), conduction by positive holes being the result of O_2 adsorption. It is interesting to note, however, that it has been possible to realise a true p–n junction in some polymers [271,320].

The electrical properties of polymers are determined by two factors: the structure of the molecule and the structure of the material. As regards molecular parameters, the necessary condition for semiconductivity in organic substances is the presence of a system of conjugated π-bonds in the molecule. As the number of π-electrons increases, we expect a decrease in ionisation potential, an increase in electron affinity [75], and an increase in polarisability, as has been established in a series of low-molecular-weight compounds with condensed rings [142]. In the case of polymers, this leads to improved electrical characteristics as the number of conjugated multiple or aromatic bonds in the polymer chain increases [45,59,61,129,133,134,167,177,214,221,253,257], and to the opposite effect when the conjugation is disturbed by lack of coplanarity of the aromatic rings [81,122,124,175,184,217,253] or by introducing into the conjugated chain aliphatic bridges, oxygen bridges, or sulphur bridges [122,124,164,165,175,176,178,180,217,319]. Pohl [172] observed an increase in conductivity with the number of aromatic π-bonds in poly(acenequinone) radicals, analogous to Eley and Parfitt's‡ rule for low-molecular-weight organic compounds [7,321,322]. Another analogy with low-molecular-weight conjugated systems — the increase in electrical conductivity§ following the introduction of nitrogen atoms into the conjugated chain [30,171,192,196,230] — is explained by the easier delocalisation of the π-electrons and also by the increased polarity of the molecules (see p. 780). The conjugated π-electron system ensures high values of the dielectric constant [29] and of the polarisability [323]. The structure of the molecule can influence the electrical properties also through changes in intermolecular interactions: introduction of side-substituents degrades the conductivity [108,110,217,228], and greater flexibility of the chain improves the electrical conductivity by facilitating intermolecular contacts [165,180,249,324].

The dependence of the electrical properties on the structure of the polymer as a whole is made evident, for example, by the improvement resulting from more ordered packing of the molecules [63,232,238] and by the effect of pressure cycling [128,130,144], both of which are attributed to changes in the properties of the intermolecular barriers [128,130,232]. On the other hand, instances have also been reported [59,61,122,175] of a decrease in resistance with decrease of the degree of crystallinity, associated with the lack of coplanarity of neighbouring condensed rings in the crystalline polymers [175] or with the break-down of the molecular crystal lattice [122]¶. On occasions, the degree of order has no particular influence on the electrical properties [57,59,178,295]. This masking of the role of the structure can be ascribed, on the one hand, to the well established competition between ordering in the material and conjugation within the molecule [165,180] and, on the other hand, to the effect of adsorbed gases.

On the question of the relative roles of order and conjugation, it is clear that greater flexibility of the molecular chains must result in closer packing and in conditions more favourable to intermolecular electron transitions, which determine the electrical properties of organic semiconductors (see Section IV). However, the introduction into the conjugated chain of groupings conducive to greater flexibility (in particular, methylene links) destroys the conjugation within the molecule and hampers the loosening of electrons. Thus, we find that single $-CH_2-$ groups introduced into the conjugated chain may increase the degree of crystallinity and improve the electrical properties by assisting intermolecular transfer, whereas longer links such as $-CH_2CH_2-$ degrade the electrical properties by lowering the degree of conjugation in spite of the fact that the degree of order is even higher [165,180]. The fact that the electrical properties are not improved indefinitely by increasing the number of double bonds in the polyene chain of a series of compounds [325,326] is further evidence that intermolecular electron transfer is the limiting stage in the conduction process.

Changes in electrical properties associated with adsorption can be identified by their reversibility.

‡ However, the electrical conductivity is reported to remain constant [64] in the series polybenzene–polynaphthalene–polyanthracene.

§ An increased conductance with partial removal of nitrogen from the polymer has been observed with poly(copper phthalocyanine) [230], but under these conditions the structure probably suffers considerable change. Weiss and coworkers [196] assume that an improvement in electrical conductivity due to nitrogen can be expected only when all the nitrogen groups exhibit either purely acceptor or purely donor properties.

¶ We should note that the more crystalline polymers are usually found to be poorer conductors than the amorphous polymers [61,122,168,175].

Adsorption effects have been demonstrated, in particular, by measurements after heating *in vacuo* [78,127,130,135,136,247,248]. Some workers have been able to ascribe changes in conductivity to a specific adsorbate: O_2,[64,78,85,176,198,229,230,259,269] H_2O,[57,181,225,239] and ethylene[196,198]. The adsorption of O_2 was found, in most cases, to increase both the resistance and the activation energy for conduction in both *n*-type and *p*-type polymers†[64,78,85,176,198,229,259], as had been previously observed with dyes. The effect of O_2 decreases with increasing temperature of preliminary heat-treatment, and the electrical properties of polymers heated above 600–800° are no longer influenced by O_2 adsorption[85,269]. Since these effects are independent of the conductivity type of the material, we can assume, by analogy with the effect of iodine adsorption on the electrical properties of polymers[198,270,271], that O_2 acts by altering the conditions for electron transfer between highly conjugated regions rather than by affecting the concentration of current carriers[85,270,271] (see also p. 778 and 779)‡.

Occasionally, however, the reversibility of adsorption effects is highly hindered[248], and in many cases changes in electrical conductance arise from the evolution of volatile bulk impurities rather than from surface desorption: the process becomes irreversible even though no structural rearrangements are involved[129,184,227]. Some workers even hold the extreme view[78,129,136,248] that in pyrolytic materials any observed activation energy for conduction significantly different from zero must be associated with adsorption processes only, and not with the true electronic nature of the polymers. However, many workers have unambiguously related changes in electrical conductivity to reversible and irreversible structural changes rather than to adsorption[47,59,61,63,122,128,130,175,225,238,269].

Heat-treatment of the polymers breaks down the molecular crystals and leads to the formation of a specific structure with a low degree of order (see p. 775): this can cause an improvement in electrical properties even at relatively low temperatures (200–400°) by favouring growth of polyconjugated regions and by strengthening their mutual interactions[47,59,61,85,121,123,157,176]. However, in the early stages of heat-treatment (up to 200–300°) this disordering process often produces an irreversible increase§ in resistance[58,110,111,133,172,179,249], sometimes even despite a concurrent increase in the conjugation within the molecule[144].

It is interesting to note that the absolute values of the thermo-e.m.f. decrease irreversibly with increase of heat-treatment temperature[127,140,145,176,272], in keeping with the general tendency for the thermo-e.m.f. to fall as the electrical conductivity rises[129,184,227,328,329].

It follows from the above considerations that a very long conjugated chain in the molecule and long-range order (or crystallinity) in the structure of the polymer are far from being essential to the development of semiconducting properties. However, a recent theoretical investigation by Little[330] has shown that a new and astonishing physical phenomenon, superconductivity at ordinary temperatures, should appear if both these conditions are satisfied (namely, the creation of a stereoregular polymer in which specially chosen substituents maintain the excited state in an ideal polyene chain, coupled with the arrangement of the molecules in a specific type of long-range order.

Some groups of semiconducting polymers show still further peculiarities in their electrical properties. In particular, the behaviour of chelate polymers is determined by factors common to all organic semiconductors (electrical characteristics superior to those of the monomer[254], influence of the ligands[221,253], exchange interactions[224]), but it is also determined by the nature of the metal[221,224,253,254,264,265,267], although the role of this factor is sometimes a minor one[138].

Many polymers with conjugated bonds show photoelectric activity[83,87,114–117,121,133,167,169,179,214,224,259,276,331–333], generally similar to the well characterised phenomena in other classes of organic semiconductors[83,116,117,169]. In most cases the photoconductivity has been shown to be electronic in origin[83,114,117]. Some anomalies have also been observed, for example, the quenching of photoconductivity by oxygen in a *p*-type semiconductor[114,116] and polarisation phenomena[169]. Unfortunately, only a few polymers show appreciable photoeffects[116].

Other characteristic features of the electrical behaviour of semiconducting polymers will be discussed in the context of conduction mechanisms (Section IV). At this stage we shall only mention the compensation effect (linear relation between E_σ and $\log\sigma_0$) observed in a number of polymers[29,64,67,167,267,334,335], low-molecular conjugated systems[67,323,325], charge-transfer complexes[7,67], and dielectrics[336,337]. According to Tal'roze and Blyumenfel'd[334,335], this relationship is characteristic only of poor semiconductors, and should not be obeyed by low-resistance polymers[121,126].

3. Static Magnetic Susceptibility and Broad-Line ESR

Many polymers with conjugated bonds show large positive values of magnetic susceptibility[104,121,160–162,184,187,190,244,246,249,303,338–340], a dependence of the susceptibility on the field[121,161,162,181,244,246,249,312,340], and saturation at relatively low fields[249,312], i.e. the properties of an antiferromagnetic below the Néel temperature[181,312]. The susceptibility increases with temperature of heat-treatment[121,181,249]. These phenomena, which have been termed "pseudoferromagnetism", usually disappear in solution[312,341], as does also the broad (hundreds of oersteds) ESR signal¶ (occasionally observed[118,187,199,227,312,342]), which becomes even broader at low temperatures and frequently corresponds to an unacceptably high number of paramagnetic centres (up to 10^{22} per gramme, or upwards of 10 per monomer unit)[342]. Similar effects have been reported for nucleic acids and their complexes with proteins[338,343,344]. It was pointed out that the compensation effect in electrical conduction should not occur in substances showing these properties[334,335].

Attempts were immediately made to relate this unusual behaviour of organic substances to the specific features of conjugated polymeric systems: in particular, to the collective interactions arising in π-electron systems of this type as a result of a particular ordered structure[29,312], or to the formation of charge-transfer complexes[338,341]. However,

† With *p*-type polyethylene subjected to radiation–thermal treatment, the specific resistance ρ and E_σ were both found to decrease[269] in the presence of O_2.

‡ Myl'nikov[259] explains the suppression of dark conduction and photoconduction caused by O_2 adsorption on a *p*-type polymer by postulating that oxygen gives rise to carrier recombination centres on the surface.

§ The increase in resistance is sometimes due to removal of impurities by the heat-treatment[129,184,227].

¶ Instances have been reported, however, in which the positive susceptibility[339] and the broad ESR signal[342] persist in solution.

Dorfman has suggested that these properties cannot be ascribed to organic structures[345,346], and must be due to contamination (by iron compounds, in particular), as has on occasions been demonstrated experimentally[203,347,348]. On the other hand, and in keeping with the view that these phenomena are not trivial in origin, positive susceptibility has been observed for polymers prepared under high-purity conditions[162,181], and the concentration of ferromagnetic impurity present has been shown to be clearly insufficient to explain the observed effects[341,349]. Hence, Blyumenfel'd believes[349] that, although the specific pseudoferromagnetic behaviour of organic compounds is associated with the presence of iron, nevertheless it is due either to a special state of the system, in which all five $3d$-electrons of the Fe^{3+} ion take part in domain formation (as in a new type of ferrite), or alternatively the behaviour is due to specific exchange interactions between the paramagnetic iron ions through the conjugated organic structure. The question of whether the static paramagnetism and the broad ESR lines are trivial in origin is still not finally settled (in contrast to the nature of the narrow ESR signal, see Section III).

The magnetic susceptibility method is used in the study of chelate polymers with paramagnetic ions to establish the structure of the chelate link[22,252,255,256] and to reveal exchange interactions through the conjugated system[224]. In the latter case, use is made also of changes in the ESR signal for chelates with metals whose ions give resonance absorption[224,263].

4. Narrow-Line ESR

Practically all polymers with conjugated bonds give a characteristic narrow ESR signal either as prepared or after further heat-treatment. As with other classes of organic semiconductors, the absorption line is a singlet†, characterised by a g-factor close to the free-electron value ($g \simeq 2.00$), of small width (ΔH from 0.5 to 15, and rarely up to 50 oersteds), and with a relatively high concentration of unpaired spins ($N \simeq 10^{16}$–10^{21} per gramme, or 1 spin per 10–10^6 molecules)‡. The temperature dependence of the signal intensity usually follows Curie's law[3,112,143,161,162,182,183,190,198,251,273], although temperature-independent signals have been reported[68,250,269]§. The width of the signal does not vary with the measurement temperature[56,112,198,251]. The signal invariably persists when the material is dissolved[3,56,68,74,83,105,185,306,312]¶, and in many cases the shape remains unchanged and the intensity decreases in proportion when the solution is diluted[3,68,74,195].

The ESR signal suffers irreversible changes as a result of heat-treatment of the polymers. The concentration of unpaired spins N increases with temperature[3,105,160,162,170,182,205,246] up to a maximum at 600–700° (for measurements made in a vacuum)[47,269,273] and then gradually falls as the temperature is raised still further, but the signal is not completely lost at 900° and even above 1000°,[85,273,275]. The line width ΔH retains its original value of 4–8 oersteds up to heat-treatment temperatures of 400–500°,[47,85,269] but it goes through a minimum (for the case of vacuum measurements) at 500–700° which can be as low as 0.5 oersted, and further increase in pyrolysis temperature broadens the signal (upwards of 10 oersteds).

Oxygen does not usually affect the ESR signal of polymers which have not been heated above 300–400°,[85,269] but a decrease in N is occasionally observed even for low-temperature specimens[44,103,203]. After heating above 300°, oxygen is found to have an effect on ΔH: measurements in air do not show a minimum and ΔH remains constant up to heat-treatment temperatures of 500–600°, beyond which the line becomes wider (as in the vacuum measurements)[47,85,123,205,269]. Bakh and coworkers[269,275] consider that the minimum in ΔH observed after heat-treatment at 500–700° is only apparent, and due to inadequate pumping off of O_2, since after thorough degassing ΔH has its minimum value (0.5 oersted) even for the lowest baking temperatures. Line broadening in the presence of oxygen probably arises from the local magnetic fields generated by the adsorbed O_2 molecules, which alter the value of the g-factor for different regions[279]. The effect of O_2 on the concentration N of unpaired spins becomes appreciable after heating the polymer above 500°, and produces a slight shift of the maximum towards lower heat-treatment temperatures (500–600° instead of 600–700°)† and a sharp decrease in N at higher temperatures. In polymers heated to 650–800° the ESR signal vanishes when measured in air[47,85,121,269], whereas with samples heated at higher temperatures[275] and some other polymeric samples[74] (measurements *in vacuo*) there is an increase in N on admitting O_2, due to the formation of charge-transfer complexes with oxygen (see p. 780). All these changes in the ESR signal are similar, on the whole, to the phenomena observed in charcoals[12]. We should stress that the differences between carbons and heat-treated polymers are arbitrary in a number of respects (see, for example, Ubbelohde[22]), and therefore it is quite likely that the ESR signal found in low-temperature charcoals is often caused not by broken bonds[12,351] but by the factors which operate in polymers with conjugated bonds and other organic semiconductors (see Sections IV and V).

The shape of the ESR line can vary from the Gaussian to the Lorentz form, depending on the conditions of pre-treatment of the polymer, the measurement temperature, and adsorption[56,68,74,123,153,195,198,269,273,275,279,293]. For low-temperature samples and low measurement temperatures the signal is of Gaussian or intermediate form, but, on raising the heat-treatment or the measurement temperature, the line gradually acquires Lorentz character[123,153,269,275]. This is consistent with stronger exchange interactions between the paramagnetic centres as the number and size of the conjugated regions are increased. Adsorbed oxygen enhances the Lorentz character of the signal by contributing to electron exchange[195,296], in keeping with the strong influence of O_2 on the electrical conductivity of low-temperature polymers[95,269] and with the analogous effect of iodine adsorption[198,270,271].

In most cases the ESR signal is a symmetric singlet, but occasionally some asymmetry is reported: with low-

† Double, or more complex, signals have been observed[105,109,161,164,190], and ascribed to isolated radicals[105]. After heating, the signal becomes a normal singlet. Hyperfine structure is sometimes revealed by measurements in solutions[56,185].

‡ Chelate polymers can give an ESR signal either because of the presence of a paramagnetic metal ion (broad line) or for reasons common to all organic semiconductors (narrow line)[224,245,250,251].

§ A decrease in the concentration of unpaired spins on cooling the polymer has been reported only once[198], and ascribed to the formation of a stable charge-transfer complex with iodine, or to the iron polychelate complex[250].

¶ Reversible loss of signal on dissolution has been reported for aniline black[203] and for polymeric charge-transfer complexes[293], as commonly observed with low-molecular organic semiconductors[350]

† Under some conditions the maximum in N can be found at very much lower temperatures[121,191].

-temperature polymers, the asymmetry arises from the ready saturation[44,56,227,279,293,306,352] due to the large spin--lattice relaxation time (10^{-4}–10^{-5} s),[49,352] but, with the highly conducting, high-temperature polymers, the asymmetry is associated with the skin effect or with the asymmetry of the g-factor[273,275]. Saturation is less marked after adsorption of oxygen[68,74,279,293] which favours spin–lattice interaction.

The ESR signal in polymers is very interesting from the point of view of their catalytic activity, since it has been possible in some cases to demonstrate a direct correlation between catalysis and the concentration of unpaired spins[39–41]. In this connection we should mention a series of papers by Berlin and coworkers on the so called local activation[41,353–356]. According to this concept, the paramagnetic centres present in compounds with conjugated bonds, and responsible for the special magnetic behaviour of materials of this type‡, excite (or activate) the neighbouring molecules and thus give rise to catalytic activity, fluorescence, dark conduction and photoconduction, and other specific properties of organic semiconductors. The mechanism of this effect evidently involves perturbation of the electronic shells of the system under the influence of the local magnetic centres, and consequently an increased probability of reaction occurring via the excited triplet state, i.e. with a lower activation energy[354,356].

III. NATURE OF THE NARROW-LINE ESR

Generally speaking, the following basic factors, which can cause the appearance of an ESR signal in organic structures of the type under discussion, are significant: (a) inorganic paramagnetic impurities; (b) organic radicals, arising either in the course of polymerisation ("trapped radicals") or during thermal degradation of the polymers ("broken bonds"); (c) stabilised double radicals, formed by the Berlin mechanism (see below); (d) the transition of molecules to the triplet state, whose level can be so low in highly conjugated systems as to be readily populated even at room temperature ($^3E_1 \simeq kT$), or even become the ground state ($^3E_1 < kT$); (e) the appearance of polar states as a result of charge-transfer processes — in particular, the formation of charge-transfer complexes; (f) the signal from quasi-free current carriers.

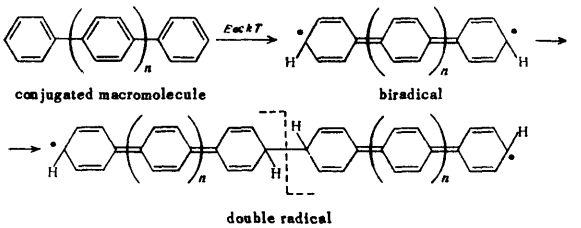
The narrow ESR signal in polymers was originally assigned to the properties of an individual highly conjugated molecule[24,29,228], and ascribed to a specific phenomenon (the appearance of some measure of unpaired character in the π-electron system at a particular stage of conjugation[29,63,245]). This interpretation is consistent with the narrowness of the line, with the dependence of the signal on the degree of conjugation in the molecule[45,84,123,176,191,306,352], with the correlation between changes in N and colour[23,175], and with the fact that the signal persists in solutions. However, many contradictions were soon discovered. Although instances of monotonic variation of the concentration N of unpaired spins with molecular weight were reported[191,207], in other cases there was no correlation between these parameters[56,84]. The observed proportionality between N and the molecular weight[68,74] cannot be reconciled on the basis of the above ideas with the fact that the length of the conjugated system does not increase with molecular weight[69]. The limited degree of delocalisation, which extends over no more than 2–7 monomer units[56,68,74,123], has been demonstrated on numerous occasions.

Furthermore, the character of the observed ESR signal did not provide an explanation of the appearance of paramagnetic centres in terms of other possible mechanisms of intramolecular excitation: either by thermal activation of the singlet–triplet transition (since the intensity varies according to Curie's law, i.e. N is independent of temperature) or due to the fact that the triplet state becomes the ground state (since the concentration of paramagnetic centres is always less than one per molecule)§.

This situation has given rise to suspicions that the ESR signal in polymers is due to impurities. However, as in the case of low-molecular organic semiconductors, we can dismiss trivial paramagnetic contaminations because: (a) all paramagnetic ions give a signal of significantly greater width[357]¶; (b) there is no analogy among inorganic para- and ferro-magnetics to irreversible temperature changes in the signal (see p. 778); (c) the signal often appears only after heating[48,168,170,323] or low-temperature carbonisation[306,340,352]; (d) the behaviour of the signal can be correlated with the colour of the material and with conjugation in the molecule[45,84,122,123,191]; (e) the signal is strongly affected by adsorption of O_2 and other substances.

At the moment, only two approaches offer a satisfactory treatment of the basic features of the paramagnetic behaviour of polymers with conjugated bonds and other organic semiconductors: Berlin's ideas on stable double radicals and the concept of charge transfer proposed by Blyumenfel'd and Benderskii.

According to the views of Berlin[15,49,84,162,359], centres which appear in the fractions of highest molecular weight are responsible for the ESR signal. Macromolecules in which a sufficient degree of conjugation is achieved (irrespectively of whether the polymerisation mechanism was radical, ionic, or molecular) can pass into the triplet state even at ordinary temperatures. The interaction between two or several such excited biradicals, termed quasi-radical polymerisation, gives a stable double radical according to the scheme



The unpaired electrons of this double radical do not interact, and do not recombine, because a mutually coplanar arrangement of the individual conjugated blocks is sterically impossible. The resulting molecular paramagnetic centres are additionally stabilised by the formation of charge-transfer complexes between the double radical and the neighbouring molecules: this, in turn, favours the excitation of these molecules to the triplet state by the local-activation mechanism (see p. 779). This explanation of the paramagnetism of polymers with conjugated bonds

‡ The nature of the paramagnetic centres is discussed in Section III.

§ This is true also of the ESR signal ascribed to the triplet state of nitrogen[182,183].

¶ Even in chelate compounds in which exchange interactions take place through organic structures[358].

evidently lacks generality, since an ESR signal can be observed also in systems where the formation of extensive conjugation chains is improbable† [122].

The hypothesis that the ESR signal in organic semiconductors is due to polar states involving charge transfer was put forward and developed in a series of papers by Blyumenfel'd and Benderskii [68,69,306,360,361]. At present, these ideas perhaps offer a more satisfactory explanation of the peculiarities of the ESR signal of low-temperature polymers [75,83,85,122,123,162,196,198,203,205,293] and of other classes of organic semiconductors [12,309,359,362,363]. According to this model, the low ionisation potential of conjugated systems assists the formation of local centres of the radical-ion type in the solid structure. The charge transfer which accompanies the appearance of these localised polar states can occur either between two neighbouring molecules, when the charge transfer is assisted by the shorter intermolecular distance, and the resulting charge-transfer complex is treated as a structural defect of the lattice, or it can involve charge capture by more remote molecules, traps, crystal defects, etc. ‡

The formation of polar states involving charge transfer is assisted by: (1) the presence of a sufficiently extensive conjugated π-electron system, which ensures high polarisability and ready ionisation of the molecules; (2) polydispersity, which produces differences in electron affinity and ionisation potential between the molecules; (3) polarity of the molecules, and in particular the presence of nitrogen atoms (which also increases the electronic heterogeneity of the system); (4) disorder and structural defects in the material as a whole, which provide the best conditions for local interactions between molecules and for the formation of traps. In the case of polymers, a special role is played by polydisperseness (as pointed out by Dulov [122] and Boguslavskii [200]), and by disorder, as evidenced by the fact that amorphous polymers are often better semiconductors than crystalline polymers [61,122,168,175]. This approach explains the contradictions pointed out on p. 779, since the formation of polar states is determined both by properties of the molecule (conjugation), and also factors less easy to characterise, such as polydispersity and structural disorder.

It should be noted that in some cases the ESR signal can arise from well known, alternative causes. In particular, the ESR signal resulting from charge-transfer complexes formed by electron transfer between a compound with conjugated bonds and an adsorbed molecule of oxygen [74,195,198,275,362,364-366] or some other molecule (see p. 774) has been specially discussed by various workers. The ESR signals sometimes observed from common radicals formed during the synthesis and trapped in the polymer structure, or from radicals of the broken bond type appearing, for example, during thermal breakdown of the polymer [105,273,367], are easily distinguished by their behaviour, since they should disappear irreversibly on dissolution or moderate heating.

In many cases (for example, in polymers heated above 900° [273] or even at lower temperatures [143]) a narrow ESR signal caused by the current carriers can be detected, similar to the signal observed in individual low-molecular charge-transfer complexes with strong binding [368-370]. Benderskii and others were able to isolate a narrow signal from photo-induced carriers in dyes, and showed that its behaviour differs from that of the broader signal associated with local paramagnetic centres [371].

IV. ELECTRICAL CONDUCTION MECHANISM

A clear description of the current-carrying processes in organic semiconductors, and particularly in polymers, is perhaps the most serious outstanding problem in the study of these interesting materials. Any mechanism proposed must explain a number of specific features of the electronic behaviour of these compounds which are now well established. The following are the most important peculiarities.

1. Electronic inhomogeneity. Measurements by various methods (a.c. measurements [200,237,243,269], studies of current noise [141] and of the effect of the adsorption of iodine [161] and of air [135], and other investigations [47,122,227,242,275]) lead to the firm conclusion that all polymers consist of discrete conducting regions (very probably, strongly conjugated or condensed regions) separated by poorly conducting (dielectric) regions evidently consisting of a disordered structure of polymer molecules (see p. 775, 776).

2. Nature of the reversible temperature dependence of the thermo-e.m.f. In most cases the thermoelectric power α is either practically independent of temperature [100,125,127,132,143,145,176,200,214,231,269,270,272] or increases at higher temperatures [100,143,145,154,176,212,229]. This suggests that the temperature variation of α and σ is the result of a change in carrier mobility at constant carrier concentration, since theory predicts a weak (logarithmic) increase of α with temperature for this type of mechanism (degenerate conductor) [14,328]:

$$\alpha = \frac{k}{e}\left[A + \ln \frac{2(2\pi m^* kT)^{3/2}}{h^3 n}\right],$$

where A is a constant which depends on the electron scattering mechanism, m^* and n are the effective mass and the concentration of the current carriers respectively, k and h are Boltzmann's and Planck's constants, and T is the absolute temperature.

When the changes in α and σ with temperature arise mainly from an exponential increase in the carrier concentration, the theory requires that α decreases with increase in temperature, in direct proportion to $1/T$: [14,328]

$$\alpha = \frac{k}{e}\left(A' + \frac{E_\sigma}{kT}\right).$$

Some polymers have shown a decrease of α with temperature [64,132,143,145,154,170,172] but the observed effect is not usually large enough to justify ascribing it to the influence of carrier concentration [64,145,172].

3. Very low mobility of charge carriers. Attempted measurements of the carrier mobility in polymers from the Hall effect have usually proved unsuccessful [48,140,157,200,225,229]. This suggests that the mobility does not exceed 0.005–0.01 $cm^2 V^{-1} s^{-1}$. Only in two cases have

† Also, a recent tentative calculation [75] shows, that the degree of polymerisation achieved (in particular) in poly(phenylacetylene) is apparently sufficient to allow transition of the molecule to the triplet state.

‡ Complexes involving partial charge-transfer can be formed [238]. Localised centres of this type do not, of course, give an ESR signal.

these measurements given positive results: poly(acenequinone) radicals gave the very low value [172,216] 0.04 $cm^2 \times \times V^{-1} s^{-1}$, and an unexpectedly high mobility (2.5–10 $cm^2 \times \times V^{-1} s^{-1}$) was observed in poly(copper phthalocyanine). However, the Hall effect measurement for the latter polymer could not be reproduced§ [225,229], and a measurement of mobility from the effect of O_2 adsorption on σ gave very much lower values [229]. Low mobility values in the polymers have been deduced also from ESR data (10^{-1}–10^{-3} $cm^2 V^{-1} s^{-1}$, [64,68,172,372]) from a.c. measurements (10^{-3}–10^{-5} $cm^2 V^{-1} s^{-1}$, [271]) and from calculations based on the band model (10^{-2}–10^{-7} $cm^2 V^{-1} s^{-1}$ [100,145,201,214]). Evidently, higher mobilities can be obtained only when the influence of the dielectric interlayers is eliminated: values of 1.4–100 $cm^2 V^{-1} s^{-1}$ have been reported [229,230,271,283,284,373]. Positive holes are usually found to be more mobile than electrons [100,140,201,208], but calculations sometimes yield the opposite result [261]. The concentrations of current carriers corresponding to the low mobilities listed above amount to 10^{12}–10^{17} cm^{-3}. [172,201,214,216,230,372]

All these special features are best explained in terms of the hopping mechanism of conduction [14,16,17,125,127,128,145,200,214,237,238,243,318], according to which current is obtained by activated hops of the carriers, over the dielectric barriers created by the disordered (non-conjugated) structures, from one polyconjugated region to the next. Under these conditions, a rise in temperature does not alter the number of effective carriers present in the polyconjugated regions (provided of course that irreversible pyrolytic processes are excluded), but it increases the probability of a jump, i.e. the mobility. As shown by the theoretical work of Klinger [374] and of Lang and Firsov [375], the hopping mechanism is the most probable in materials of low carrier mobility, in which the current is carried by small polarons and difficulties arise in the measurement of the Hall effect. This mechanism explains also the characteristic temperature variation of α of the majority of polymers, and the results obtained, in measurements with a.c. [200,237,238], with stretching and compression of a heat-treated polymer [128].

According to the band mechanism [117,154,172,328], the intermolecular π-electron interactions give rise to a conduction band which is common to the whole volume of the polymer, and in which the concentration of carriers depends on the energy needed to extract an electron from the π-conjugated system and transfer it to the quasi-free, conducting state. In other words, the carrier concentration is determined by the width of the forbidden gap, and increases with temperature. From the point of view of the band theory, a low mobility is the result of narrow bands (large effective carrier mass). However, this mechanism is inapplicable to the majority of polymers because it is inconsistent with the temperature variation of α [64,71,100,125,127,132,143,145,176,212,214,229,231,269,270,272] and with the extremely low mobility, corresponding to an improbably small mean free path (less than 1 Å) [17,140,214,230] and to unacceptably large effective masses of carriers [140]. Furthermore, the band model is particularly improbable for polymeric materials, which usually lack a crystalline structure [376] (although calculation has shown [377,378] that strict ordering is probably unnecessary to give rise to an electronic band structure in polymers). Nevertheless, there are cases, such as when the mobility is greater than 1 $cm^2 V^{-1} s^{-1}$, or when α decreases with temperature (see below for the strong carrier–carrier interaction which sometimes arises under these conditions, giving rise to pseudometallic conduction [372]), and also in photoconduction processes [48], where the band mechanism can be applied with some reservations [143,183]¶.

The tunnel mechanism [7,64,78,135,136,158,232,248] assumes that the true activation energy for conduction E_σ (ignoring the effects of adsorption, cross-linking, etc.) is determined by the energy needed to transfer an electron to an excited level in the molecule, so that E_σ in polymers with conjugated bonds should be small and tend to vanish as the degree of conjugation in the macromolecule is increased. The magnitude of the conductivity is limited by the probability of non-activated intermolecular tunnelling of the electrons, which is itself largely determined by the thickness and shape of the intermolecular barriers. The effectiveness of tunnelling transitions is proportional to the concentration of electrons in excited levels, itself an exponentially increasing function of temperature. With polymers, in contrast to low-molecular organic semiconductors and individual charge-transfer complexes [14], it is difficult to confirm the correctness of the tunnel mechanism by comparing E_σ with optical data [98,99], but is has been done [64]. Some workers [232] have postulated a tunnel mechanism on the grounds that the experimentally observed curve of activation energy *versus* the degree of crystallinity (which determines the shape of the barriers) agreed with the calculated curve. Others, however, have adopted this mechanism without sufficiently convincing evidence [78,135,136,248]. The tunnel mechanism seems hardly likely to be generally applicable to polymers with conjugated bonds, because the objections raised against it, even in the context of low-molecular organic semiconductors (to which it can be applied with much better justification [376,383]), are very cogent in the case of polymers, in particular, the much lower probability of the tunnel mechanism than of the hopping mechanism in substances with a low carrier mobility [375]. It is also interesting that the very small activation energies for carrier generation within the conjugated region (0.1 eV approximately) have been confirmed experimentally by a.c. measurements [268], but these same measurements have shown that the rate of the d.c. conduction process is limited by a stage attended by a considerable activation energy (of the order of 1.0 eV), i.e. probably by barrier jumps between conjugated regions.

Thus, the hopping mechanism appears to be the most plausible for the majority of typical polymeric semiconductors†. However, in some groups of polymers the electrical conduction is known to arise by different mechanisms. In particular, when the mobility exceeds 10 $cm^2 V^{-1} s^{-1}$ (i.e. for high-temperature samples [85,273], for compositions

§ The high mobilities in this case can probably be ascribed to the participation of the *d*-orbitals of the copper atom under favourable steric disposition of the molecules, as has been demonstrated for the monomeric copper phthalocyanine [266].

¶ It may not be out of place to point out that recent Hall effect and conductivity measurements on inorganic semiconductors (NiO and CoO) have shown that the band model is applicable to these oxides [379,380], although the hopping mechanism had been previously postulated on account of their low mobility [381]. Some recent calculations [382] of a number of electrical parameters of organic semiconductors have given grounds for retaining the band concepts for systems of this type.

† An alternative view, recently put forward, is that the electrical behaviour of semiconducting polymers is determined by the superposition of two activated processes: changes in the concentration of current carriers and changes in their mobility [175,242], as had already been proposed for organic semiconductors of low molecular weight [383,384].

with a high metal content[231], or when strong charge-transfer complexes are formed with polymers[271]), and also when α is found to decrease steeply with temperature[132], the electrical conduction is probably quasi-metallic as a result of strong electronic interactions in the polymer. Under these conditions the carrier concentration can be appreciably higher than normal (up to 10^{19} cm^{-3}). [143,273]

The chelate polymers form another special group, in which metal ions play an essential role. The specific features of the electrical properties of polychelates have been explained by invoking the ligand field theory[254], the resonance of structures involving a metal[265], or (by analogy with ferrites) a mechanism in which the electronic jumps depend on the variable valence of a metal ion[265].

V. RELATIONSHIP BETWEEN ELECTRICAL AND MAGNETIC PHENOMENA AND GENERAL THEORIES OF SPECIFIC EFFECTS IN ORGANIC SEMICONDUCTORS

A superficial comparison might lead to the conclusion that in general there is no correlation between the electrical conductivity σ and the paramagnetism of polymers with conjugated bonds. In the first instance, the irreversible temperature changes in σ and in the concentration of unpaired spins N, which occur during pyrolysis, are different (except after low-temperature heating, when the changes are in the same sense): σ increases continuously, whereas N goes through a maximum (see p. 777 and 778). But even when the changes are monotonic, an increase in σ by many orders of magnitude corresponds to an increase in N by a factor of only several tens or hundreds[64,122,214]. Secondly, the reversible temperature variation of the width of the ESR signal, in accordance with Curie's law, suggests that N stays constant, whereas σ has a positive temperature coefficient (see p. 775 and 778). Thirdly, in most cases N is greater than n (the concentration of current carriers)[64,143,214,273]. (See also Tobin's calculation[372] based on the results of Hatano and coworkers[63]; see p. 778 and 780.)

However, a deeper study of the problem reveals a correlation between the electrical and magnetic properties.

(a) Despite the fact that in most cases there is no quantitative correspondence between N and n (i.e. that the ESR signal is not, in fact, given by the current carriers), a distinct correlation is very often observed between changes in N and changes in electrical properties on heating in the low-temperature region[85,170,205,227,269], during chemical reactions[45,111], as the degree of crystallinity is increased[63], on changing the extent of conjugation[64,122,177], and for photo-induced electrical and paramagnetic characteristics[52,69]. In some groups of related polymers a direct proportionality between N and $\log\sigma$ has even been observed[122,214].

(b) The existence of a close association between the semiconductor properties and the ESR signal is suggested also: firstly, by the temperature independence of both N (Curie's law) and n[143,273] (see p. 780), and, secondly, by the success achieved in explaining the electrical behaviour of polymers by applying the ideas of polar states and charge-transfer complexes (see p 779) and of local activity centres (p. 778). The studies of polymers treated with halogens[174,198,205,211,289] provide the best example of this, since in every case the authors were able to correlate the improvement in electrical characteristics with the formation of charge-transfer complexes. The same conclusion probably applies in every other reported case of decrease in resistance and in activation energy E_σ following introduction of halogens[17,261,290] or metal salts[48,51] into the polymers. Karpacheva[174] obtained a direct demonstration that the maximum concentration of paramagnetic centres in the bromine and iodine complexes of polymeric Schiff's bases occurs at the same composition as the minimum activation energy for conduction E_σ and minimum resistance. A monotonic increase in photoelectric activity with concentration of paramagnetic centres was observed in a study of the local activation effect[69,356,385]. Further evidence for a close link between electrical conductivity and charge-transfer complexes is provided by the decrease in E_σ with increasing polarity of the molecules[314] (see p. 780).

(c) In polymers which have been heated to sufficiently high temperatures the concentration n of current carriers can become equal to the concentration N of unpaired spins[143,274]. Under these conditions the strong electronic interactions give rise to quasi-metallic conduction (see p. 781), and the ESR signal is obviously produced by the conduction electrons[143,273]‡. On further raising the pyrolysis temperature, the increasingly strong electronic interactions can lower the effective concentration of unpaired spins (and even cause the ESR signal to disappear altogether, see p. 778), so that N becomes smaller than n.

Thus, we are forced to the conclusion that the electrical and magnetic properties of polymers are by their very nature closely interrelated, although the relationship is a complex one, and can be masked by various subsidiary phenomena.

Not surprisingly, in view of the fact that comparison of the properties of other groups of organic semiconductors has led to a similar conclusion[361,368,369,385,386], attempts have recently been made to evolve generalised theories of the electrical and magnetic effects in organic semiconductors. We refer first and foremost to Blyumenfel'd and Benderskii's[360,361,378] theory of polar states already mentioned above (p. 779), which is primarily concerned with the formation and dissociation processes of local paramagnetic centres, and to Pohl's ion–exciton model[17], which deals mainly with the mechanism of current transport§. The local activation concept developed by Berlin and coworkers also aims to unify the nature of electrical and magnetic phenomena in organic semiconductors, and has already been mentioned on p. 778 and 779.

Blyumenfel'd and Benderskii consider that the electrical and magnetic properties of organic semiconductors are determined by the activation energy of a polar state within the crystal, i.e. by the concentration and also by the nature of the local paramagnetic centres, consisting of defects in the crystal structure. Generation of charge carriers

‡ This mechanism of the generation of an ESR signal is similar to that demonstrated by Wagoner for high-temperature charcoals[386], but our polymers (unlike the latter materials) show a strong variation of signal intensity (i.e. of N) with O_2 adsorption, which has no effect, however, on the electrical conductivity[85,269]. Hence, it is doubtful whether the ESR signal in polymers which have been heated only a little above 800° is in fact caused by conduction electrons. These considerations have led to the suggestion[85] that electrical conductivity arises not only from unpaired electrons, but also from delocalised, strongly interacting electrons (or holes) which do not give an ESR signal.

§ Pohl's discussion deals specifically with ionic conduction, but his arguments are equally applicable to current transport by electrons and holes, which has been proved to exist in organic semiconductors (see p.775 and Ref. 5).

occurs by dissociation of the polar state by the normal exciton mechanisms[8,387]. For very weak intermolecular interactions, the levels of the polar states lie well above the ground state of the system, and therefore the concentration of polar (paramagnetic) centres is very small and the materials should be diamagnetic and insulating. In compounds of this type, which includes low-molecular organic semiconductors and possibly also poorly conducting polymers, the ESR signal can arise only from charge-transfer complexes, formed by the reaction between molecules of the main constituent and easily ionised non-paramagnetic impurities (in particular, high-molecular fractions). As the interactions in the solid become stronger, the levels of the polar states shift downwards, with an increase in the concentration of intrinsic paramagnetic centres able to generate an ESR signal as a result of electronic transitions between molecules of the matrix. In these compounds (among which we classify some strong, individual charge-transfer complexes and many highly conducting polymers) we expect to find a relationship between electrical and paramagnetic characteristics. When the intermolecular bonds are strong enough, the levels of the polar states can become practically indistinguishable from the unexcited level, and in this case the paramagnetic state becomes the ground state of the system. Substances of this kind should exhibit a characteristically temperature-independent paramagnetism and high conductivity, like the better individual charge-transfer complexes based on tetracyanoquinodimethane[389]. However, when the levels of the polar states are shifted even lower, the radical-ions formed by electron transfer can behave as independent paramagnetic centres (Curie's law), and the resistance should rise again (as in ionic crystals); this situation may exist in the charge-transfer complexes involving halogenoquinones[388,390]¶. Unfortunately, the theory of polar states, though it offers a satisfactory description of the paramagnetism of organic semiconductors, does not underline sufficiently the specific aspects of the conduction mechanism, since it examines charge transfer essentially from the standpoint of the exciton band model.

According to Pohl, whose approach is based on the concept of ion pairs[391], the molecules of an organic semiconductor form chains (or groups) of ion–exciton complexes of the type $(M^+M^-)\ (M^+M^-)\ \ldots\ (M^+M^-)_x$ in which electronic excitation and electron transfer are greatly facilitated by the strong exciton–exciton and ion–exciton interactions. Hence the steady-state concentration of excited electrons in the system can be quite high, and this will increase the probability of electron exchange between these polymeric forms of excitons by the activated jump mechanism. On the whole, this model describes satisfactorily the special features of the electrical behaviour of organic semiconductors, but unfortunately Pohl does not consider the concrete mechanisms of intermolecular interactions in molecules of various types, nor does he accord special attention to the properties of exciton–ion complexes as paramagnetic centres in organic semiconductors.

Although the nature of the special electrical, magnetic, catalytic, and other properties of organic semiconductors is still far from clear, there can be no doubt that in the last few years this class of organic compounds has attracted exceptional interest from physicists and theoretical chemists. Thus, we may hope that the next few years will witness the appearance of a unified theory of the electronic effects in organic semiconductors, which will make it possible to understand the true nature of the specific properties of these remarkable compounds and to control those properties by rational methods.

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The above review of the experimental results for and of the theoretical models of semiconducting polymers, in conjunction with published work on other groups of organic semiconductors which could not be discussed here, justifies the following conclusions.

1. All organic semiconductors (polymers with conjugated bonds, one-component conjugated systems of low molecular weight, charge-transfer complexes, biological materials, and charcoals) have in common a group of special properties which distinguishes them from most of the ordinary organic compounds: this is particularly true of their electrical, magnetic, catalytic, and also some other characteristics.

2. The peculiar behaviour of organic semiconductors arises, on the one hand, from the presence of conjugated π-bond systems in their molecules, and, on the other hand, from specific features of the solid-state structure of these compounds (in the case of polymers the presence of electrically conducting highly conjugated regions separated by dielectric layers).

3. Although a unified interpretation of the nature of the paramagnetism in organic semiconductors is still lacking, we can now assert that the most common cause of a narrow ESR signal in these materials is the presence of paramagnetic polar states (in particular, charge-transfer complexes) whose formation is very considerably assisted by the properties of the system of conjugated π-bonds. A special case is provided by charge-transfer complexes involving adsorbed molecules of oxygen, or charge-transfer complexes into which molecules of halogens or of some other materials have been introduced.

4. The most satisfactory explanation of the special electrical behaviour of organic semiconductors relies on the activated hopping mechanism, although in some cases (compounds of low molecular weight, and individual charge-transfer complexes) the band model also can be applied.

5. The problem of the basic common origin of electrical and paramagnetic phenomena in organic semiconductors is not finally settled, but in many instances we have convincing proof of a correlation between these properties, and some of the theoretical concepts already put forward may lead to a unified explanation of the special electrical and magnetic behaviour of organic semiconductors.

¶ Admittedly, it becomes difficult in the latter case (level of polar states below ground level) to explain the fact that the experimentally determined concentration of the paramagnetic form in organic semiconductors is almost invariably less than 100%.

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