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Electrical and Photoelectric Properties of Organic Polymeric Semiconductors

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I. INTRODUCTION

Organic compounds containing systems of conjugated multiple bonds are now termed organic semiconductors: the conductivity of these substances is electronic, increases exponentially with temperature, and is greater (as a rule) than the conductivity of normal organic compounds.

During the past 10 years, in addition to extensive studies of the semiconducting properties of low-molecular-weight organic compounds, we have witnessed a significant volume of work on the synthesis and characterisation of a new class of organic semiconductors: the macromolecular compounds. The rising interest in semiconducting polymers is due, on the one hand, to recent advances in the physics and technology of inorganic semiconductors, which have led to a search for new materials showing semiconductor properties, and on the other hand to the successful preparation of polymers with a wide variety of physicochemical properties, resulting in widespread applications of polymers in technology. The attractive prospect of developing simple models, leading to a deeper understanding of some biophysical processes (which take place, as a rule, in complex macromolecular systems) has undoubtedly been an additional stimulus to developments in the physics of electronic phenomena in organic systems.

The present review deals with the most important experimental and theoretical data relating to organic semiconducting polymers having an electronic (as distinct from an ionic) conduction mechanism. Since studies on low-molecular semiconductors have led the way to an understanding of the semiconductivity of polymers, we shall briefly review the basic ideas of organic low-molecular semiconductor physics without attempting to cover the literature in detail. The later sections will discuss, separately, the electrical properties of organic semiconducting polymers and photoelectric processes in these materials.

We thought it desirable to devote a whole section to the photoelectronics of organic polymers because the subject is of very recent origin (5 years at the most), and has not so far been reviewed in any way. The aim of this review is to familiarise the reader with the physical aspects of organic polymeric semiconductors.

II. LOW-MOLECULAR-WEIGHT ORGANIC SEMICONDUCTORS

The following basic laws have been shown to apply[1-8] to low-molecular-weight organic semiconductors (dyestuffs, aromatic hydrocarbons):

1. The dark conductivity (σ_d) varies with temperature (T) according to the law

$$\sigma_d = \sigma_0 \exp(-E_d/2kT)\dagger \qquad (1)$$

where σ_0 is a constant for the particular semiconductor, k is Boltzmann's constant, and E_d is the thermal activation energy for dark conduction. E_d usually varies between 0.5 and 3 eV, and the value of σ_d at room temperature can vary between wide limits (10^{-1}–10^{-20} ohm^{-1} cm^{-1}). The thermal activation energy for dark conduction corresponds to the energy of the long-wave edge of the optical absorption curve, and decreases with increasing number of π-electrons in the molecule.

† The form of the exponent depends on the conduction mechanism assumed.

2. Ohm's law is obeyed, in general, up to fields of 10^3 V cm^{-1}, beyond which the current increases faster than linearly with voltage.

3. Polymorphic modifications of a given compound can have substantially different conductivities and activation energies for conduction, and charge carriers of different sign[9,10]. There is evidence of conduction anisotropy (anthracene) in different crystallographic directions.

4. The conductivity increases with increase of pressure up to 100 kg cm^{-2}, but not beyond.

5. Carrier mobilities in organic low-molecular-weight compounds are usually very low (< 1 cm^2 V^{-1} s^{-1}). Hall mobility data for organic semiconductors are extremely rare owing to serious difficulties in the measurement of the Hall effect (the high ohmic resistance of the compounds and possibly also some specific aspect of the conduction mechanism). More recently, a pulse method of measuring mobility in a "sandwich" type of cell has come into use. By this method it has been shown that the mobility in anthracene increases on lowering the temperature, suggesting the possibility of applying the band model (in which this dependence is ascribed to a decrease in the concentration of scattering centres with decrease of temperature).

6. Impurities and defects have a considerable effect on the semiconducting properties of organic semiconductors, but the results of different workers show large discrepancies.

7. The thermoelectric power is independent of temperature, suggesting that the free carrier concentration is independent of temperature.

8. The photoconductivity spectra (particularly in thin layers) and the photo-e.m.f. spectra are usually very similar to the absorption spectra. In thicker layers the photoelectric sensitivity decreases at the absorption maximum. Many experimental results show that a highly developed surface or defects must be present before photoconductivity can appear. These observations suggest that charge carriers are formed either at the surface, when an exciton diffuses towards it, or by the simultaneous interaction of a molecule with two photons or two excitons.

9. The relaxation time of the photoeffect varies over a wide range, from 10^{-6} s to tens of minutes.

10. The photoconductivity (σ_{ph}) increases exponentially with temperature (T) according to the law

$$\sigma_{ph} = \sigma_0 \exp(-E_{ph}/kT) , \qquad (2)$$

where σ_0 is a constant for a particular semiconductor and E_{ph} is the thermal activation energy for photoconduction. The value of E_{ph} usually falls between 0.1 and 0.3 eV, pointing to the presence of bound states from which the carriers must be thermally activated in order to move in the applied electric field. The nature of these states is not fully clear.

11. Current carriers can be injected into organic crystals from various electrodes.

12. The sign of both light and dark carriers in most organic semiconductors so far examined corresponds to positive holes.

13. Vapours and gases can have an appreciable effect on the conductivity and photoelectric sensitivity of the semiconductors.

14. The quantum yield of the photoeffect is not large (10^{-1}–10^{-7} electrons per quantum).

15. Changes in photoconductivity have been observed in a weak magnetic field[11,12].

16. The possibility of forming charge-transfer complexes enables the electronic parameters of the semiconductors to be varied between wide limits.

17. On the basis of the experimental facts listed above, the mechanism of semiconductivity in low-molecular-weight organic compounds is usually associated with overlap of the wave functions of π-electrons from neighbouring molecules. Two basic approaches are usually followed. Some authors have attempted to apply to organic semiconductors the band model which satisfactorily describes electronic phenomena in inorganic semiconductors. Others support the "relay" or "hopping" mechanism of conduction. The distinguishing feature of molecular organic semiconductors is the fact that the interaction forces between separate molecules (van der Waals forces) are much weaker than the interaction forces between the component parts of each molecule, so that the molecules can retain their individuality in the crystal lattice. This gives rise to the exciton type of light absorption, and to the formation of narrow bands of singlet and triplet states in the crystal. These exciton states are satisfactorily described by molecular wave functions rather than by the one-electron Bloch functions used in the band theory. Excitons are neutral entities, and can only be treated as transition states in the formation of free carriers. However, these states are important in conduction when an electron migrating through a crystal can be treated as bound to one of the molecules or missing from it. The nature of these states is determined by the specific features of the lattice of a particular organic semiconductor. An analogous approach can clearly be used to discuss high-molecular weight organic semiconductors, to which the remaining sections are devoted.

III. ELECTRICAL PROPERTIES OF ORGANIC SEMICONDUCTING POLYMERS

The conductivity of organic polymeric semiconductors increases exponentially with temperature according to Eqn. (1). Historically, the earliest publications on organic polymeric semiconductors related to materials obtained by pyrolysis. The electrical conduction of pyrolysed polymers was first observed by Kmetko on heat-treated cellophane[13] and by Winslow and coworkers[14,15] by pyrolysing poly(divinylbenzene) and poly(vinylidene chloride)[14,15].

When organic compounds are heated to 400–650°C, high-molecular-weight compounds are formed from highly unsaturated aromatic molecules[16]. When the temperature is raised still further, large planar networks of atoms packed in fairly random piles are formed, and at very high temperatures (3200°C) these condense into large, highly ordered planes and produce the graphite structure. Thus, graphite can be considered to be the limiting case of a polymeric semiconductor. In spite of fairly detailed studies of these compounds, fully satisfactory mechanisms for the change in their electrical properties with structure and heat treatment have not yet been put forward[17]. Materials prepared at temperatures in excess of 1200°C are usually classified as polymeric carbons. At room temperature, polymeric carbon is an n-type semiconductor with a very narrow forbidden gap (0.07–0.01 eV). The conductivity type changes with temperature, which may be ascribed to the presence in the polymeric lattice of valency-unsaturated non-bridging carbon atoms. Because of this unsaturation, electrons can be extracted from the inner carbon atoms with formation of positive holes as current carriers[18,19].

Materials prepared by heat treatment up to 1200°C are normally classified as pyropolymers. They are usually characterised by a narrow forbidden gap. There have been reports of pyropolymers with conductivities covering the

range from semimetals to dielectrics (10^3–10^{-13} ohm^{-1} cm^{-1}), of n- or p-conductivity type, and mobilities between 10^{-6} and 100 cm^2 V^{-1} s^{-1}.[20]

Pyropolymers prepared from organic compounds containing atoms of oxygen, nitrogen, chlorine etc. are particularly interesting. Among the first semiconducting polymers, and the most thoroughly investigated, are the compounds obtained from poly(acrylonitrile)[21]. Published results[21-27] justify the conclusion that electrical conduction in pyrolysed poly(acrylonitrile) is determined by an ionic and an electronic contribution. The ionic contribution, which accounts for the conductivity of the initial polymer, is predominant in specimens prepared at 150–300°C, and decreases with increasing temperature of heat-treatment. At the same time the electronic contribution increases, as required by the increasing number of conjugated double bonds. The increase in electrical conductivity resulting from treatment at 400°C is due to an increase in the effective mobility of current carriers, not to an increase in carrier concentration. Studies of the temperature dependence of electrical conductivity and of thermoelectric power have led to the conclusion that the regions of polyconjugation in poly(acrylonitrile) specimens treated at low temperatures have the properties of impurity semiconductors, changing to semimetal properties as the temperature of heat-treatment is raised. The unpaired electrons which are manifest in the ESR spectra behave as donor impurities[28-30]. It has been shown that the value and the temperature dependence of the electrical conductivity are determined essentially by activated jumps between polyconjugated regions, whereas the thermoelectric power is characteristic of the polyconjugated regions themselves. Estimates of the carrier mobility give values of the order of 10^{-3} cm^2 V^{-1} s^{-1}. These results were obtained by assuming that the band theory can be applied to the system. Although the validity of the band model as applied to organic polymers is by no means established, experiment shows that the formalism of this model gives a fairly consistent picture of the mechanism of charge transfer when applied to poly(acrylonitrile). Work[31,32] on the effect of hydrostatic pressure and tension on the resistance and thermo-e.m.f. of poly(acrylonitrile) filaments is particularly interesting. It was shown that the concentration of free carriers remains constant on raising the pressure, whereas the activation energy of electrical conduction decreases. It follows that the change in conductivity with temperature is determined by the activated nature of the mobility and is associated with the height of the potential barriers separating the regions within which electrons are delocalised. Longitudinal extension increases the distance between molecules and should therefore increase the height of the potential barriers, lower the mobility of the current carriers, and increase the resistance, as is experimentally observed. Kustanovich and coworkers[33,34] have shown that the electrical properties of pyrolysed filaments of poly(acrylonitrile) are determined by gases adsorbed on the surface: this suggests that results obtained in the presence of air should be critically re-examined.

In principle, results obtained on pyrolysed polymers should be difficult to interpret because the structure of the resulting products is usually poorly characterised, and there can be no doubt that heat treatment leads to the appearance of new formations which behave as impurities and are difficult to control. In this context, it is interesting to note reports[35,36] of changes in the electrical properties of poly(acrylonitrile) under the influence of infrared radiation.

An extensive series of papers by Berlin and coworkers and by other authors is devoted to the electrical and magnetic properties of polymers containing acyclic conjugated systems (polyvinylenes)[37-46] and polymers with aromatic rings in the conjugated chain[47-56]. These workers examined the change of conductivity with temperature, and its relationship to paramagnetic absorption and to the structure of the polymer. Most of the polymers investigated had fairly high resistivities ($\sigma_d < 10^{-7}$ ohm^{-1} cm^{-1}) and gave an electronic paramagnetic absorption signal with a g-factor corresponding to the free electron. In spite of the considerable effort devoted to studies of the relationship between the ESR signal and the electrical properties of highly conjugated polymers[37-39,50-72], the relation between current carriers and the concentration of paramagnetic centres is still far from clear. Blyumenfel'd and Benderskii ascribe the ESR signal and the electrical conductivity to the formation of polar charge-transfer complexes either between two neighbouring molecules or by the trapping of charge at a crystal imperfection[57-64]. Another approach is based on the suggestion by Berlin[65-68] that high-molecular-weight fractions containing stable biradicals are formed during the synthesis or the subsequent heat treatment, and that these are the source of current carriers.

Many workers have studied the influence exerted on the semiconducting properties by polymer structure, both supermolecular (crystallinity, degree of order, etc.) and molecular (chemical structure of the macromolecule itself). As a rule, the electrical conductivity increases on increasing the number of π-electrons in the molecule and when atoms with electron-donating properties are introduced into the chain[73-77]. When groups or heteroatoms which interrupt the conjugation are introduced into the macromolecule, the electrical conductivity decreases as a result of the increased activation energy for conduction[50,53,78-84]. Experiments with poly(phenylacetylene) have shown that the activation energy for dark conduction is independent of the molecular weight and corresponds to the radiation maximum in the luminescence spectra[61,62]. This is evidence for the generation of carriers by thermal ionisation of luminescence centres.

However, the electrical properties of polymers depend not only on the degree of conjugation in the macromolecule but also on the physical structure of the polymer. Hatano and Kambara[85,86] found that the resistance of crystalline polyacetylene is lower than that of the amorphous material by 5–8 orders of magnitude. It should be noted, however, that the oxygen content was rigidly controlled in this work. The electrical properties of a series of chelate polymers were shown to be determined, in the first instance, by the degree of order in the polymer and by the nature of the electronic interactions, rather than by the structure of the individual macromolecule[87,88]. The conductivity can be raised by introducing into the macromolecule groups tending to make it more flexible and thus favouring denser packing[54,87,89,90]. Many workers have noted conduction anisotropy with respect to the alignment axis of the macromolecules[28,29,31,91,92], an increase in conductivity with pressure[93-95], and a major influence of adsorbed vapours and gases on the electrical conductance (particularly oxygen)[42,87,96-101]. The effect of oxygen on the electrical conductivity involves either a change in the concentration of current carriers or a modification of the height of the potential barriers between macromolecules or polyconjugation regions. Most high-resistance polymeric semiconductors show a linear dependence (compensation effect) of the activation energy E_d on the logarithm of the pre-expo-

nential factor σ_0 in Eqn. (1)[48,57,58,102,103]. Sazhin and coworkers[104-107] have studied the temperature dependence of electrical conductivity and its relationship to supermolecular structure on a series of polymeric dielectrics.

Compounds containing a metallocyclic ring in the main chain form an important group of semiconducting organic polymers. Poly(copper phthalocyanine) was synthesised by Epstein and Wildi[108-109]. The resistivity of the polymer at room temperature is 10 orders of magnitude lower than that of non-polymeric copper phthalocyanine (10^7–10^8 ohm cm). Interesting Hall effect measurements are reported in the same paper, from which valuable conclusions may be drawn as to the conduction mechanism. It is found that the change in resistance with temperature of a polyphthalocyanine which has not been heat treated reflects both a change in mobility and a change in the carrier concentration. The mobility value was 10 $cm^2\ V^{-1}\ s^{-1}$, and it is interesting to note that it was obtained by direct measurement (Hall effect). Indirect methods of measuring mobility in polymers usually yield values many orders of magnitude lower. Direct methods of measuring mobility (such as the transit-time method) also give low values in polymers (10^{-3}–10^{-4} $cm^2\ V^{-1}\ s^{-1}$)[110]. The Hall constant for polyphthalocyanine heat-treated at 450°C did not change with temperature, pointing to a constant carrier concentration. In this case the activation energy for electrical conduction can be identified with the mobility activation energy.

Berlin, Frankevich and others also investigated polyphthalocyanines[96,97,111-114]. They noted a strong effect from vacuum and oxygen treatment on the electrical properties of the samples, and proposed a method for measuring carrier mobility in polymers by simultaneously monitoring the desorbed acceptor molecules and the electrical conductivity of the polymer[96]. They find that copper polyphthalocyanine is an *n*-type semiconductor with a mobility of 10^{-2} $cm^2\ V^{-1}\ s^{-1}$ and a concentration of current carriers of 10^{18}–10^{19} cm^{-3}.

Polymeric chelate materials with semiconductor properties have been prepared also from tetracyanoethylene[115-127]. By measuring electrical conductivity at high frequencies it was found that the resistance and the activation energy for electrical conduction decrease with increase of frequency. Hence, the barriers between macromolecules must be taken into account when discussing the conduction mechanism[119-121]. Polymeric chelate compounds are among the most promising materials for technological applications. In polymers of the coordination type we can expect high mobilities and broadening of the energy levels into wide bands. Semiconducting chelate polymers have been prepared from ferrocene[16,48,128-131], poly(vinyl alcohol)[32] and other compounds[77,133-144].

A large group of semiconducting polymers consists of compounds with conjugated triple or cumulative bonds in the main chain[145-163]. A poly-yne with the appearance of a black powder containing 98% of carbon and retaining the structure of polyacetylene up to 200°C has been prepared and investigated[146,152,153]. The polymer shows *n*-type conduction, the donor centres being copper atoms included in the molecular carbon chain of the polyallene structure. On raising the temperature of heat treatment the polymer changes conductivity type, which the authors ascribe to thermal dissociation and removal of copper and hydrogen atoms from the carbon chain. Under these conditions the terminal carbon atoms behave as electron acceptors. Infrared and X-ray diffraction analysis[147-153] have shown that these carbonaceous products of acetylene condensation are open forms of carbon in which linear macromolecules with a poly-yne and partly a cumulene structure are aggregated in molecular packs of parallel carbon chains. Some of the macromolecules are "cross-linked" into a spatially disordered conjugated polyene structure. Studies of the electrical properties of poly-yne derivatives before and after heat treatment, in cases where the structure consists of parallel molecular chains aggregated into packs with a high degree of azimuthal order[148,149], have shown that these materials also are semiconductors.

Radiation-thermal treatment of polymers appears to be a promising method of preparing materials with semiconducting properties[92,164,165]. For example, the method has been used to prepare semiconducting materials from polyethylene[70,98,165-169], with conductivities between 10^{-14} and 10^2 $ohm^{-1}\ cm^{-1}$, activation energies for conduction between 0 and 1.5 eV, and thermoelectric power between 1 and 500 $\mu V\ deg^{-1}$. Ohm's law is obeyed up to fields of 10^3 V cm^{-1}. At the boundary between low-pressure polyethylene and polyethylene subjected to radiation-thermal treatment, *p*–*n* junctions have been obtained with a rectification ratio of 10 in the region of 400–600 mV[165]. The model adopted for the conduction mechanism involves polyconjugation regions 50–100 Å long alternating with barriers 5–20 Å thick which determine the activation energy of the conduction process[98]. Current rectification has been observed also at the junction between polyethylene crystals and metals[170].

The formation of charge-transfer complexes between a polymer and electron-donor molecules[98,102,168,169,171-185], resulting in an increase in conductivity by 4–6 orders of magnitude, offers very attractive possibilities for the preparation of low-resistance polymers. In addition to the compounds mentioned above, semiconducting materials which have been investigated include those prepared from poly(diphenyldiacetylene)[186], polypyrroles[187], polybutadiene[188], poly(azophenylenes)[189], polyaniline[190,191], poly(vinyl acetate)[192] and various other materials[103,193-199]. The semiconducting properties of organic polymers (in the dark) have been discussed in a number of review articles[16,99,102,200-208]. Lastly, we shall note that proteins and nucleic acids have been shown to have quite specific electrical properties of the semiconductor type in a number of investigations[209-224] which cannot be discussed in detail in the present article.

IV. PHOTO-SEMICONDUCTING PROPERTIES OF ORGANIC POLYMERS

Whereas studies of the electrical conductivity, thermoelectric power and ESR spectra of organic polymers are relatively abundant, reports of photoelectric phenomena in organic macromolecular compounds began to appear only during the past 5 years, and are far from numerous. We must stress that the study of photoelectric processes in polymers gives a fuller description of electronic phenomena in these systems than is available from studies of electrical conductivity, since a light beam allows us to probe strictly defined energy states of the electrons. Furthermore, the photo-semiconductors (which behave as insulants in the dark) become accessible to study. These materials are of interest in electrophotography—the only technological area in which organic photosemiconductors have yet found a genuine practical application. It is significant that the number of patents on electrophotographic layers made from organic materials is ever increasing. The patent literature dealing with this subject has been reviewed by Sidaravichyus[225] and by Newman[226,227]. The

most widely used electrophotographic layers are those of poly(vinylcarbazole). However, their physical parameters have been investigated and they have been found to be a hundred times less sensitive than such inorganic materials as selenium sensitised by zinc oxide[228-232]. On the other hand, they have a high resolution (absence of grain structure) and higher contrast than is found in selenium, they are unaffected by the material and size of the substrate, they are technologically attractive, and they offer a number of other advantages. The best promise of improving the sensitivity of organic polymer layers lies in the addition of chemical sensitisers[233] and in the search for new materials[234,235].

The formation of photoelectrically sensitive materials by u.v. irradiation of the copolymer of vinylidene chloride (85%) and vinyl chloride (15%), known as Saran Wrap, was first reported by Oster and coworkers[236,237]. The photoconductivity was attributed to the formation of free radicals under illumination because conditions which induce or eliminate the ESR signal affect the photoconductivity in the same sense. It should be noted that the preparation of polymeric materials with semiconducting properties by irradiation with monochromatic light has some important advantages over alternative methods such as pyrolysis: (1) by appropriate choice of wavelength, it is possible to initiate chemical reactions selectively; (2) the light beam can be confined to particular areas of the target. By virtue of these effects, Oster and coworkers were able to prepare p–n junctions at the interface between differently irradiated areas.

The search for photoelectrically sensitive polymers has been pursued by the present writer for many years in A. N. Terenin's laboratory. Approximately 400 organic polymers have been examined so far [poly(phthalocyanines), polyphenylenes, poly(cyanamides), poly(acetonitriles), polyferrocenes, poly(phenylacetylene) and its copolymers, polymers of malonic and adipic acid, stilbene polymers, poly(vinylphthalimides), polymers of quinizarine with metals, many different chelate polymers, etc.].

Some of these materials, when tested for d.c. photoconductivity, showed a small increase in conductivity with a slow relaxation when illuminated, but it was not possible to distinguish a photoelectric effect unambiguously from the bolometer effect.

By using the capacitor method of photo-e.m.f. measurement[238] with modulated light (300 Hz), polymers with a photocurrent relaxation time of 10^{-2} s were found, and the photoelectric processes in these compounds were examined in detail[100,239-252]. The polymers in question were compounds with triple bonds[239] and poly(metal acetylides)[240]. The compounds were synthesised in Korshak's laboratory by Sladkov and coworkers[145-154,253-256]. An internal photoeffect was observed in 50 of the 70 compounds examined, whose structure can be represented by the formulae

$$R'\!\left(-C\equiv C-R-C\equiv C-\right)_n R'; \quad R\left(-C\equiv C-\right)_n R,$$

where R and R′ are organic radicals containing functional groups or hetero-atoms. The polymers are finely divided powders of colour varying from white to black, poorly soluble or quite insoluble in organic solvents.

Under illumination, the capacitor photo-e.m.f. is observed in the u.v. or visible region of the spectrum[239,243]. In the most of the poly-ynes, the photocurrent carriers have a positive sign. Previous irradiation of the polymers with u.v. light has been shown to increase the photo-e.m.f. This effect is ascribed to ionisation of the conjugated molecules under the influence of u.v. light and formation of centres acting as traps for the photo-electrons. This mechanism is confirmed by some preliminary experiments by the ESR method[249,250]. With poly(pp'-diethynylazobenzene) at 77°K, a partially reversible ESR signal photo-induced by u.v. light can be observed. By comparing the behaviour of the ESR signal with that of the photo-e.m.f. under u.v. light we conclude that the photo-induced ESR signal is due to the capture of photoelectrons by the positively charged local centres formed in the polymer structure by the action of u.v. light. The spectral distribution of photo-e.m.f., measured on a number of polymers, is characterised by smoothly increasing curves (towards higher energies) with a threshold at 2.0 eV.

The dark resistance of the poly-ynes is 10^{12}–10^{14} ohms, decreasing by 2–3 orders of magnitude under the light of a mercury lamp[242,249]. The variation of the photocurrent i_{ph} with illumination (L) is of the form $i_{ph} = \alpha L^n$, where n can vary between 0.5 and 1.0. The photocurrent is proportional to the voltage raised to the power n, where $n > 1$. A typical range of relaxation times for the photocurrent in poly-ynes is between 10^{-5} s and several seconds. From the initial rise and decay of the photocurrent we can extract an exponential component with a time constant of approximately 10^{-5} s.[241] We should stress that poly-ynes and polyacetylides are the only polymers for which such short-lifetime photoconduction processes have yet been reported. With time constants of this order there can be no doubt that the photo-effect in these polymers is electronic in nature. After the initial exponential stage, the relaxation of photoconductivity changes to a hyperbolic law in a time interval of between 10^{-5} s and several seconds[241].

As for the photo-e.m.f., the spectral distribution of the photoconductivity in poly-ynes and of the influence of u.v. light on these materials was investigated[242]. The photoconductivity spectra are displaced towards longer wavelengths as compared with the photo-e.m.f. spectra. The main photoconductivity maximum for poly(pp'-diethynylbenzene) is found, as in most other photoelectrically sensitive semiconductors, beyond the edge of the absorption curve, pointing to a difference between the rates of surface and volume recombination of the photocurrent carriers. The activation energy for poly(pp'-diethynylazobenzene), measured from the photoconductivity spectrum, was 1.82 ± 0.02 eV. The same value was recently obtained in Japan for the activation energy of dark conduction in this polymer[162]: this suggests that the same electronic transitions are responsible for both the dark conduction and the photoconduction in the polymers. As with the photo-e.m.f., the photosensitivity of poly-ynes undergoes a partially reversible change under the influence of u.v. light. Spectrally [with poly(pp'-diethynylazobenzene), say] this change consists in a redistribution of the ratios of the intensity maxima in the photoconductivity spectrum and a shift towards longer wavelengths of the short-wavelength maximum. The change in photoconductivity under u.v. irradiation, like the change in photo-e.m.f., is associated with the capture of the photoionisation electrons by the resulting traps, as shown by the ESR measurements discussed above.

Using the copolymer of p-diethynylbenzene and p'-nitrophenylacetylene, the absorption spectra in solution and in thin film form have been compared with the photoconductivity spectra. Photoconduction is observed in the absorption band of the polymer, and its trend is similar to that of the absorption spectrum[243].

A photoeffect has been found in 15 poly(metal acetylides)[240,250] having a chain structure expressed by the general formulae R–C≡C–M and M–C≡C–R–C≡C–M,

where R is an organic radical and M is a metal (Cu, Ag). Most of the work was done on copper derivatives, and in particular on poly(copper phenylacetylide), abbreviated CPA. These polymers are insoluble, fine powders of different colours, from yellow to dark red, and are coordination compounds[245]. The poly(copper acetylides) had a resistance of 10^9–10^{10} ohm in the dark, decreasing to 10^7–10^8 ohm on illumination with monochromatic light. Growth of the photocurrent to the steady-state value was accomplished in 10–15 s. As with the poly-ynes, the variation of the photocurrent with illumination is given by the formula $i_{ph} = \alpha L^n$, where n varies between 0.5 and 1. Ohm's law is obeyed up to fields of 10^2 V cm^{-1}, beyond which the photocurrent increases faster than linearly with applied voltage. The sign of the photocurrent carriers in all the poly(copper acetylides) is positive[240].

A comprehensive study of the spectral distribution of photo-e.m.f., photoconductivity, absorption, and luminescence in CPA has been described[245]. The photo-e.m.f. spectrum was found to be similar to the absorption spectrum, but the photoconductivity spectrum is displaced towards the long-wave region as compared with the others and has a maximum beyond the absorption edge. The latter fact denotes an important contribution from surface recombination of the carriers, arising from an extensive system of surface states. The increase in photo-e.m.f., accompanied by a decrease in luminescence yield, due to previous illumination, was investigated spectrometrically but remains puzzling.

Work done so far justifies the assumption that the absorption, photoeffect, and luminescence maxima in CPA are similar in nature. The bands are characteristic of fundamental electronic transitions in the polymer. Migration of charge carriers in CPA is assisted by the lowering of the potential barriers between molecules caused by π-complex bridging between the electron-acceptor copper atoms and the acetylene bonds. Changes in the luminescence and photoeffect spectra under u.v. irradiation are due to the rupture of weak coordination bonds in the polymer, which alters the relationship between polymer homologues. Bond breaking facilitates the dissociation of excitons at the resulting defects, leading to an enhanced photoeffect and a lower luminescence yield. This mechanism is supported by numerous experiments on the luminescence of CPA at 77°K[245], in which it was shown by spectroscopic measurements that the degradation of CPA under u.v. light proceeds up to the stage of formation of isolated molecules of diphenylbutadiyne dispersed throughout the polymer structure. Under these conditions we may postulate energy transfer from the semiconducting substrate (CPA) to the diphenylbutadiyne molecules.

Vapours and gases can strongly affect the semiconductor properties of polyacetylides[100,244]. Dry oxygen produces a reversible decrease in the electrical conductivity and photoconductivity by 3–2 orders of magnitude, and lowers the photo-e.m.f. by a factor of 3–5, which is unusual for a p-type semiconductor such as CPA. Gas adsorption on a semiconductor surface may lead, in the first instance, to the formation of a double layer resulting from the adsorbed molecules, and secondly to the creation of new recombination centres or trapping levels. An investigation of the effect of oxygen on the spectral distribution of photosensitivity has identified the quenching effect of oxygen with the formation of effective recombination centres which decrease the lifetime of majority carriers (holes). The recombination centres created by oxygen are primarily surface states, as shown by special experiments on the effect of u.v. light in vacuum, in which it was found that oxygen is photodesorbed from the CPA surface in a vacuum[100,248].

Water vapour reversibly suppresses the electrical conductivity and photoconductivity, and enhances the photo-e.m.f. of CPA[244]. The effect of water vapour on the photosensitivity spectrum has been examined, and shown to be associated with the formation (following adsorption) of an electrical double layer on the CPA surface, resulting from capture of the majority carriers (holes) on surface states.

Electron-acceptor molecules such as quinone and chloranil in the gas phase did not appreciably affect the photo-e.m.f., but suppressed the photoconductivity and the conductivity of CPA[249]. When the specimen was exposed to these molecules in solution, the photo-e.m.f. increased by an order of magnitude but its spectrum did not change appreciably. Evidently, new centres are formed by contact with the solvent, and these enable the quinone molecules to be adsorbed and act as electron traps owing to their high electron affinity. The presence of highly developed surface states, indicated by the above results on the effect of gases and vapours on the electrical properties of CPA, implies catalytic activity towards oxidation reactions[251].

From the view point of applying the concepts of semiconductor physics to biological polymers, some curious results have been obtained in a study[252] of the effect of nucleic acids and amino-acids on the photosemiconducting properties of CPA. In particular, it was shown that deoxyribonucleic acid and ribonucleic acid increase the conductivity and photoconductivity of the polymer by 2–3 orders of magnitude without affecting the spectral sensitivity. The photo-e.m.f. is increased several-fold. An investigation of the effect of purine and pyrimidine bases, which enter into the composition of nucleic acids, showed that only adenine exhibits the effect. The mechanism of these phenomena is probably similar to the process which has been termed chemical sensitisation in inorganic semiconductors[257]. It should be noted that studies of the interactions between biological polymers and model synthetic polymers have opened up new pathways for investigating the specific biological properties of these compounds.

The mechanism of the photoeffect in polymers is probably as follows. The primary act consists in the excitation of a molecule by the absorption of a photon[239,249,250]. The excited state (or exciton) migrates until it collides with a structural or chemical defect, on which a pair of free photocurrent carriers is formed. The electron is retained by the positively charged centres, but free holes can migrate through the entire system of macromolecules. In CPA it would appear that pair formation does not require an activation energy, as shown by the temperature dependence of the photoconductivity at very high frequencies[258]. Potential barriers at the boundaries between macromolecules can be expected to limit the photoelectric sensitivity of the material very markedly. Hence the role of random bonds associated with cross-linking of the macromolecules becomes important.

An effect not previously observed in organic semiconductors—the spectral sensitisation of the photoeffect by dyes—has been found and spectroscopically investigated in poly-ynes and polyacetylides[246–250]. The effect is well known in inorganic semiconductors[259,260], and consists in the appearance of photoelectric sensitivity in the absorption band of a dye adsorbed on the surface of a photoconductor. The sensitisers used in conjunction with poly-ynes and polyacetylides include Methylene Blue, Pinacyanol, chlorophyll, phthalocyanines, erythrosine, hematin, Rho-

damine B and others. The sensitised photoconductivity spectrum and photo-e.m.f. spectrum are similar to the absorption spectrum of the dye in solution (10^{-3} M), which suggests that the monomeric form of the dye takes part in the sensitising act. Dimers and more highly aggregated forms of the dye also take part in the sensitising process. Because of the influence of adsorption forces, the sensitised photosensitivity spectra are displaced by 10–15 nm as compared with the absorption spectra of the dyes. The effectiveness of spectral sensitisation can be as much as 30–40% of the intrinsic photoelectric sensitivity. Adsorption of the dye alters the intrinsic photoelectric sensitivity of the polymeric substrate. For example, the intrinsic photo-e.m.f. was increased by a factor of 30 by adsorption of erythrosine. A detailed study of the spectral curves for intrinsic and sensitised photoeffects (photoconductivity and photo-e.m.f.) has been made using Methylene Blue, chlorophyll *a*, and Pinacyanol. With Methylene Blue it was shown, by a spectrometric method, that the efficiency of spectral sensitisation is a maximum at a solution concentration of the dye of 10^{-3} M. The sign of the photocurrent carriers is the same in the intrinsic and in the sensitised region. The results indicate that the sensitised photoeffect in organic semiconductors follows the same pattern as in inorganic semiconductors. Dyestuffs of the most diverse classes—strong electron acceptors such as Methylene Blue, and readily oxidised compounds such as chlorophyll—are equally effective in sensitising the photoeffect in organic semiconductors. Dyes of the following types are found to act as sensitisers: cationic (Pinacyanol, Methylene Blue), anionic (erythrosine), and neutral (chlorophyll, phthalocyanine, hematin), some of which belong to the photographic sensitiser class (Pinacyanol) and others to the desensitiser class (Methylene Blue). As with inorganic semiconductors, sensitisation occurs through the monomeric, dimeric, and higher polymeric forms of the dye. Some of the dyes examined as sensitisers do not themselves show photoelectric sensitivity in the solid phase, but those that are photoelectrically sensitive show a large increase on adsorption. Therefore, the most likely sensitisation mechanism involves energy transfer from an excited dye molecule to electrons in the filled band or on levels close to it and promotion of these electrons to empty traps, thus promoting the free motion of positive holes. Data obtained from ESR and data on the influence of vapours and gases on the photoelectric properties of polymers suggest that these localised traps are mainly on the surface. The observed change in the intrinsic photoelectric sensitivity of the polymer is related to the nature of the traps generated by the adsorbed dye.

The phenomenon of chemical and spectral sensitisation of the photoeffect, recently described for poly(vinylcarbazole)[261] and polyacenaphthylene[262], is analogous to that found in polyacetylenes. The high photoelectric sensitivity of poly-ynes and polyacetylides has enabled these materials to be made into electrophotographic layers of sensitivity comparable to that of inorganic photosemiconductors[234].

Bradley and Hammes[263,264] have reported photoconductivity in thin (~ 1 μm) organic layers produced by polymerisation in the glow discharge of monomers containing nitrogen, sulphur, selenium, and certain metals. Irradiation with unfiltered white light raised the room-temperature dark conductivity (which was of the order of 10^{-17}–10^{-13} ohm^{-1} cm^{-1}) by a factor of 10^3. The activation energy for photoconduction in these films is 0.25 eV, pointing to thermal activation with formation of free carriers from excited molecules in an intermediate, non-conducting state, rather than band-to-band transitions. All the polymers gave short-circuit photocurrents, evidently due to a photovoltaic effect at the interface between the film and the transparent electrode. The charge carriers were identified as electrons from the polarity of the photocurrent.

It is interesting to note that addition of a trace of iodine during polymerisation in the discharge increased the electrical conductivity and photoconductivity by three orders of magnitude. The authors point out that their results are characteristic of amorphous organic semiconductors in general rather than of any specific polymer structure. The importance of this observation is obvious if we remember that the authors did not control the composition or the structure of their films, produced by polymerisation in a discharge. Clearly, it is impossible to discuss the observed semiconducting properties in terms of the structural parameters of the macromolecule or of the sample as a whole. However, systems of this type can already be of practical interest. For example, these films have been used successfully as high-temperature photodetectors (up to 200°C).

Rozenshtein, Davydov, and others observed photoconductivity in polymeric Schiff's bases made from benzil and *p*-phenylenediamine[265], polyazines[266,267], and poly(diphenyldiacetylenes)[268]. The activation energy for photoconduction in these compounds was shown to lie between 0.1 and 0.3 eV. With poly(diphenyldiacetylene) the activation energy for photoconduction was found to increase with wavelength of the light, due to the existence of an energy distribution of trapping levels. The intensity–current characteristic is of the usual form ($i_{ph} = \alpha L^n$), with n lying between 0.5 and 1. Ohm's law is obeyed up to field intensities of 10^2–10^3 V cm^{-1}. All the polymers have a resistivity higher than 10^{12} ohm cm in the dark. The poly(Schiff's base) gave appreciable photopolymerisation effects, making the interpretation of results difficult.

Drabkin and Rozenshtein proposed the use of the photoconductivity method to investigate changes taking place during heat treatment of polyacrylonitrile[269]. By comparing the time–temperature curves for the increase in the number of conjugated bonds with those for the photoconductivity the authors were able to show that the formation of conjugated bonds is a sufficient condition for the onset of electronic conduction on the polymer. However, it has been stated[36] that photoconductivity in polyacrylonitrile is possible even without conjugated bonds. In particular, photoconductivity was demonstrated in a complex between the polymer (not heat treated) and dimethylformamide solvent. These results point to the need for careful removal of the last traces of solvent from polymer films before attempting to examine the films. The many conflicting data reported by different workers on the semiconducting properties of the same material may be due to varying specimen purity. On the other hand, the formation of charge-transfer complexes between donor-acceptor molecules and polymers is a very promising way of lowering the resistance of polymeric materials and increasing their photosensitivity[180–184,233,270,300].

A group of workers have synthesised poly [1,3-diphenyl-5-(4-vinylphenyl)-2-pyrazoline][271] and polyacenaphthyls and their nitrile derivatives[272], and studied their photoconductivity. The photoconductivity spectrum of the first polymer[271] is reported in the region from 300 to 600 nm. The superlinear law relating the photocurrent to illumination ($n = 1.2$) reported by these workers is unusual in organic semiconductors. Some of the polymers examined have proved useful in electrophotography.

A report by Drechsell and Görlich[273] of photoelectric sensitivity in a polyvinylene film, prepared from poly-(vinyl alcohol) by elimination of water in the presence of dehydrating agents, is noteworthy. The Hall constant of the resulting material was measured, and used to calculate the carrier density (of the order of 10^{16} cm^{-3}) and mobility (10^{-3} cm^2 V^{-1} s^{-1}). The conductivity type was electronic. This polymer is of interest primarily as a possible infrared detector, since photoconductivity occurs in the region of 0.6–6.4 μm according to the photoconductivity spectrum published by the authors. Mrosowski and coworkers[274,275] had previously suggested the possible use of pyrolysed films of cellophane or poly(acrylonitrile) as infrared detectors. However, their results do not show unequivocally that the observed effect was not bolometric.

Beck[101] discusses the photoconductivity of polyphenylene and polyvinylenes. At room temperature, and depending on the polymerisation conditions and on the oxygen content, the observed resistivities fell in the range 10^{1}–10^{15} ohm cm, with activation energies between 0.025 and 0.96 eV. A small decrease in resistance was observed in the unfiltered light of a filament lamp. In the discussion of the kinetics of the photocurrent the author distinguishes between a primary (fast increase in photocurrent with time of irradiation) and a secondary photoeffect (long-term increase in photocurrent). According to Beck, the primary photoeffect corresponds to the $^0E \rightarrow {}^1E$ transition, and the secondary photoeffect to the $^1E \rightarrow {}^3E$ transition, where ^0E is the ground state of the molecule, ^1E is an excited singlet state, and ^3E is a triplet state of the molecule. This distinction is evidently unjustified, since there are no grounds for identifying the excited state of the molecule with the state giving rise to conductivity. Even less justified is the conclusion that the secondary photocurrent is associated with a triplet state of the molecule. The so-called secondary photocurrent is due, in all probability, to the physical condition of the polymer and to defective contacts. Beck[101] proposes a tunnel mechanism for the transition across molecular potential barriers, and gives an estimate of 0.6 cm^2 V^{-1} s^{-1} for the carrier mobility.

A photoeffect has been observed in polyethylene under the action of u.v. light[276,277]. The quasi-classical method of calculation of the ionisation potential of polyethylene in the solid state gives a value of 4.5 eV. Absorption spectral studies revealed the presence of structural and impurity absorption, but no threshold was found in the region of 4.5 eV. The observed photo-e.m.f. and photoconductivity are probably due to impurities, and further work is needed to explain the nature of charge carriers and traps in this material. The mechanism of formation of free charges in polyethylene is likened to charge separation in an assembly of n–p–n structures connected in series. The extent to which such a mechanism can be justified is not yet clear. We note that photoconductivity has been observed also in the radiation-thermal treatment products of polyethylene[167,278].

Photoelectric sensitivity in biological polymers has been observed in an extensive series of investigations[221,224,279–282]. Liang and Scalco observed photoconductivity in adenosine[279], in the sodium salt of deoxyribonucleic acid[280,281], and in polyglycine[286]. The sodium salt of deoxyribonucleic acid had an anomalously high thermal activation energy for photoconduction, 0.9 eV, as compared with the values commonly observed in organic semiconductors. The authors ascribe the high activation energy for photoconduction to the existence of two contributions: (1) the energy required to generate free carriers, and (2) the energy which the carrier must have in order to overcome the potential barriers opposing its motion. We should note that the light source used by these workers—a tungsten filament lamp—had an energy maximum at about 1 μm, whereas the materials examined have an absorption maximum in the u.v. region, showing that the observed photoconduction is due to impurities. The nature of the photoconductivity (whether ionic or electronic) has also not been finally established. Nelson[221] observed photoconductivity in hemoglobin and in gelatin stained with dyes. He suggested that, following light absorption by the protein, energy is transferred by a radiationless resonance mechanism to the dye, which acts as the most easily ionised centre. Studies of photoelectric phenomena in biologically important polymers are only just beginning, and they cannot fail to yield important information on the properties of these polymers in the near future. The writer believes that combined investigations of the photoeffect and luminescence in these compounds will be the most valuable in this field.

A decrease of resistance under illumination is reported in a number of papers dealing with organic polymers, besides those mentioned above. The phenomenon is mentioned in the case of polyacene quinone polymeric radicals[73], poly(*p*-diethynylbenzene)[156], chelate polymers[88], polyazopolyarenes[283], poly(tetrafluorethylene) irradiated by X-rays[284], and others[285]. Extremely interesting work has been reported also on the photoelectric sensitivity of polydisperse organic systems with dyes in the polymer matrix[286,287], or inorganic ions and semiconductors[288].

V. CONCLUSIONS AND PROSPECTS

The vast fund of data on the electrical phenomena taking place in organic polymeric semiconductors, accumulated during the past 5–8 years, is indicative of the rapid development of this branch of knowledge. It must be admitted, that serious obstacles exist to further scientific progress and to the large-scale penetration of these materials into technology. From the scientific point of view these difficulties arise primarily from our uncertain knowledge of the structure of most of the materials examined. This is specially true of polymers prepared by pyrolysis, radiolysis, and similar methods. During the modification of the starting polymers by these methods, far-reaching structural changes undoubtedly occur. Yet, only very few papers deal with the structure of the macromolecule and with the physical structure of the final product. As a rule, authors confine themselves to a statement that their materials have a heterogeneous structure with polyconjugation regions separated by unspecified barriers. Views regarding the size, crystallinity, degree of packing etc. of these formations are extremely hazy. In spite of this, far-reaching conclusions are drawn as to the relationship between the chemical structure of one macromolecule and the electrical properties of the polymer as a whole: in these circumstances, such conclusions are hard to justify. It should be noted that even attempts to correlate the semiconductor properties of low-molecular organic semiconductors (dyes) with the specific chemical structure of their molecules have encountered serious difficulties[289,290]. It is now well established that supermolecular structure is the decisive factor which determines the specific photosemiconducting properties of dyes, whereas the molecular structure (presence of π-electrons) leads only in principle to the appearance of semiconductor properties[9,10,291].

The position is slightly more favourable with polymers prepared by direct synthesis, since in most cases the

chemical structure of the macromolecule is accurately known. But even with these materials the inadequacy of the information as to the role of the physical structure of the resulting polymers in determining their semiconducting properties is readily apparent. Little is known of the influence of defects and foreign impurities on the semiconducting properties of organic polymers. Inorganic semiconductor materials with prescribed properties became available only by rigorous purification followed by doping with the correct impurities. Some problems in solid-state electronics have been solved only by preparing inorganic semiconductors with a total impurity content of 10^{-9}–10^{-10}%. With organic semiconductors, the figure (in the most favourable cases) is higher by 8–9 orders of magnitude.

Thus, whilst not denying the value of a search for new semiconducting organic polymers, the writer believes that there is an urgent need for more detailed studies of their specific physical structure from the point of view of solid-state properties. It is obvious in principle that a periodic chain consisting of carbon atoms attached to an equal number of hydrogen atoms must have an electronic spectrum with allowed and forbidden energy bands. If hydrogen atoms in the chain are replaced by side-groups, the latter can play the part of impurities. Electropositive or electronegative substituents can be treated as acceptor or donor impurities respectively. In contrast to covalent crystals, in which impurity atoms can take up or give up one or several electrons, fixation or emission of a fractional electronic charge is possible in our systems. Transfer of a complete charge may require the cooperation of several bonds acting in the same sense. Many defects of various kinds, found in polymers, can also play the part of donor or acceptor impurities.

As the previous discussion shows, there are essentially two possible charge-transfer mechanisms: the hopping (or jumping) mechanism and the band mechanism. The low mobility values in polymers are a strong argument [292-297] in favour of the former mechanism, which consists of a series of consecutive, activated jumps by the current carriers from one macromolecule to the next. The activation energy for conduction in this case defines the probability of these jumps, and a temperature rise may be thought to increase either the effective mobility or the effective concentration of the current carriers. If the energy barriers are sufficiently permeable, there is also a finite probability of non-activated tunnelling transition by the electrons. According to theoretical work, the hopping mechanism is in principle incompatible with observation of the Hall effect: this may be the reason for the many failures to detect a Hall effect in polymers.

The band model assumes that the charge carriers move in generalised energy bands available to all the π-electrons in the polymer. The width of these bands decreases as the overlap of the wave functions of the π-electrons decreases, and in the limit the bands shrink to conduction energy levels or, in the terminology of the band model, to a very large effective mass of the charge carriers. The band model is based on the strict periodicity of crystalline materials, with allowance for the potential of a real crystal in determining the effective mass of the current carriers. However, many of the polymers in question are amorphous or largely heterogeneous materials. Thus a great deal of interest attaches to the possible application to these systems of the theory of liquid and amorphous semiconductors, in which the electronic properties are determined by short-range rather than by long-range order [296,297]. It has been shown on more than one occasion that long-range order is a sufficient but certainly not a necessary condition for the formation of energy bands [296,297].

Useful results have been obtained also by combining the ideas of the hopping and the band mechanism when dealing with the heterogeneous structures of organic semiconducting polymers. The band model is applicable to an individual macromolecule or to the polyconjugation regions, since these are strictly regular systems, and the conduction electrons can be treated as perfectly free. On the other hand, the migration of charge carriers between macromolecules or regions of polyconjugation is best described by the hopping mechanism.

Pohl introduced the concept of eka-conjugation [73,74] to describe a type of electron delocalisation for which even at room temperature the number of excited states is considerable. He estimates that eka-conjugation will appear if 10–15 pairs of conjugated bonds are present. The nature of the excited states is discussed in terms of excitons and ion–exciton complexes, mutually interacting, and thus substantially assisting the transfer of charge carriers.

In any case, we must remember that the number of organic semiconducting polymers is already of the order of one thousand, and is increasing all the time. It is obviously unreasonable to expect a single theory of electrical conduction to apply equally well to them all.

The problem of the generation of photocurrent carriers in organic polymeric semiconductors is also not finally resolved. By analogy with low-molecular organic semiconductors [1-8,60,64], the photoeffect is assumed to be a multi-stage process [239,248,249]. The primary step is the formation of a singlet or a triplet molecular exciton. These excitons give rise to transfer excitons (two ions) or to a free pair of carriers, either spontaneously or by interaction with defects or other excitons. The latter process depends on the relative contribution of the hopping and the band conduction mechanism. Direct optical transitions to conduction states are improbable under these conditions, which explains the absence of these particular bands in the absorption spectra of the condensed phase.

In addition to an increased concentration of current carriers, envisaged in the above mechanism of carrier generation, we can assume in principle that the role of light is to lower the potential barriers between individual macromolecules or polyconjugation regions. As a result, the effective conductivity increases. This mechanism may operate in polymers whose carrier concentration is unequivocally temperature-independent. The formation of non-equilibrium carriers can also lead to a lowering of the barriers through their polarisation effect. Both processes (increase in concentration and change of barrier height) will then operate together. It should be noted that a detailed analysis of the mechanism of photocurrent generation in semiconducting polymers is complicated by the insolubility (or poor solubility) of most of the compounds examined. Thus, the absorption spectra of the individual macromolecules (in solution) cannot be compared with the absorption spectra and photoeffect of polymers of uniform molecular weight in the condensed phase, which would offer valuable information on collective interactions in polymeric semiconductors. Hence, the development of synthetic routes to soluble semiconducting polymers is a problem of the first importance. At the same time, this approach would clarify the role of intercrystalline and other defective layers, which at present have a major effect on the results since much of the work has been done on compressed discs or powders. There is little doubt also that the availability of soluble polymeric semiconductors would have important repercussions in thin-film electronics.

In general, the problems involved in the practical application of organic semiconductors are of interest for their own sake, and much could be written about them. We wish to state the following. When organic polymers were first introduced into electronics, their basic role was that of insulators. With the appearance of semiconducting polymers, these materials are now considered as potential technological material for semiconductor electronics. Furthermore, the problem of developing materials showing superconducting properties at room temperature[298,299] on the basis of conjugated systems has now been formulated and is being studied. This broad field of applications for polymeric materials is not fortuitous: it derives from the extreme variety of their physicochemical properties and of the methods available for modifying them. Whilst the superconductivity concept has met serious objections, both experimental and theoretical, and needs to be extensively reconsidered, there can be no doubt about the application of semiconducting polymers. The first steps in this direction have already been taken with the preparation of electrophotographic layers[225-234]. Their main shortcoming at the moment is a relatively low photosensitivity, but as was mentioned above there are some effective methods of raising the sensitivity by introducing chemical and spectroscopic sensitisers into the polymers. Radiation detection from the vacuum u.v. to the far infrared becomes possible in principle by using these systems.

The position as regards the application of organic semiconductors is reminiscent of the 1920-1930's, when practical uses for inorganic semiconductors were first suggested. It should not be forgotten that almost 30 years had to elapse before inorganic semiconductors could make an impact on technology over a broad front, whereas studies of organic polymeric semiconductors go back less than 10 years.

Also, there is a tendency to use organic semiconductors as a direct replacement for inorganic semiconductors. In view of the specific properties of the organic materials, this is not always the best approach. Thus, we know that the most successful uses of inorganic semiconductors (in transistors, detectors of various kinds, etc.) depend on the high mobility of charge carriers which characterises these materials. Organic semiconductors, on the other hand, are inferior in this respect. Hence, we must look for specialised areas of application. One possibility is in the electronics of low currents. In organic semiconductors, non-linearity of the current–voltage characteristics sets in at relatively low fields (10^2–10^3 V cm^{-1}), and the materials can be used as non-linear elements (rectifiers, varistors, thermistors, etc.). In conjunction with photochemical methods, they can be used to develop new printing processes. A valuable property of these materials is their ability to transmit excitation, which may find application in entirely new systems of information transmission. As the nature of elementary processes in organic semiconductors becomes clearer, we can look forward to a better understanding of various facets of physical processes in living organisms (mechanism of photosynthesis, energy migration and storage processes in biological systems, carcinogenic activity, catalysis by ferments, colour vision, etc.).

The main problem in the physics and chemistry of organic polymeric semiconductors is the preparation of materials with prescribed electrical properties. Recent advances in polymer synthesis, and the use of newer and more rational physical methods of structure modification, justify the hope that the problem will be solved. There can be no doubt that, as our understanding of electronic processes in organic polymeric semiconductors becomes deeper, ever-widening fields of application in science and technology will be discovered.

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