Conductivity and Superconductivity in Polymers*

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1 Introduction

If an electrically conductive polymer is to find technical applications it should be flexible and capable of being shaped by normal processes. The first conductive polymers were mostly refractory pyropolymers resembling graphite, but more recent work has shown that conduction can be obtained in other structures which are more amenable to plasticization. Some of these enjoy modest commercial success, but dramatic improvements to produce polymers with metallic conductivity and even superconductors depend on our gaining a greater understanding of conduction mechanism in polymers.

To economize in our use of polymers we need to tailor them more closely to our requirements. This is particularly true of polymers which, by conducting electricity electronically, do not become exhausted in use like ionic conductors and yet are more flexible and lighter in colour than the conductive mixtures of carbon black with conventional polymers.

Thus an electrically conducting polymer should conduct electronically like a metal, have good mechanical properties, and be normally processable. No such polymer has yet been made but the way is gradually becoming clear and one or two useful conducting polymers are just appearing on the market.

Progress in this field depends on understanding how organic materials conduct. We shall say a little about this, then consider the two broad classes of conductors and finally discuss superconduction.

No really satisfactory theory of organic conduction has yet emerged but the picture is taking shape and we see that it is the molecular nature of organic solids which dictates their electrical properties.

2 Molecular Conductivity

Semiconductors fall between metals and insulators (Figure 1) and have conductivities ranging from 10^{-10} to 10^{+2} ohm^{-1} cm^{-1}. The conductivity (σ) depends on the concentration of charge carriers (n), their charge (e), and mobility (μ) according to equation (1). The concentration of carriers (electrons), and hence the semiconductivity, increases with temperature according to a Boltzmann-type distribution with activation energy E_A [equation (2)]. Thus semiconductivity with a positive activation energy is distinguished from metallic conductivity which falls as the temperature rises.
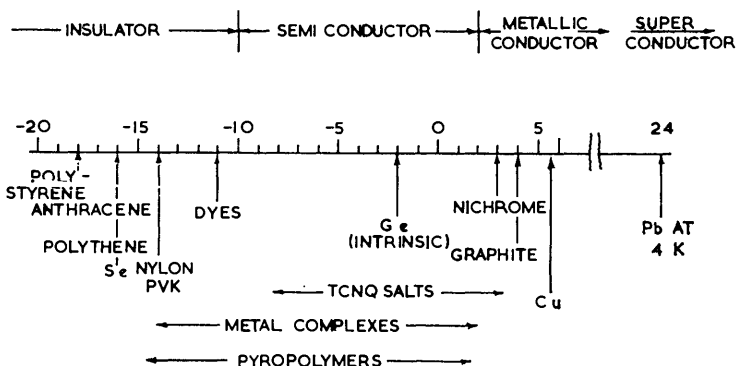
Figure 1 *Conductivity ranges of various types of material. The scale gives the log of the conductivity* (ohm^{-1} cm^{-1}) *at* 300 K

$$\sigma = ne\mu \tag{1}$$

$$\sigma = n_0 e\mu \exp(-E_A/kT) \tag{2}$$

Two distinct transport mechanisms are often considered: band conduction and hopping conduction. In a solid with long-range order and closely packed atoms, as in a metallic semiconductor, the energy levels form conduction and valence bands separated by an energy gap. An electron on excitation into the conduction band leaves a hole in the valence band which also acts as a charge carrier and as the carriers move freely in the bands they have high mobilities. This is occasionally the case with close-packed molecular solids such as anthracene which, with a mobility of *ca.* 1 cm^2 V^{-1} s^{-1} ($\mu \sim 1$), is almost a band-type conductor but, having no charge carriers, is an insulator. Most organic molecules are widely separated, being held together by weak van der Waals forces. Hence the electronic coupling between organic molecules is poor and herein lies the major obstacle to conduction as it is difficult for an electron to pass between them. Electrons then move by thermally activated hopping and because they spend a long time on each molecule mobility is low.

Generally, mobility increases with long-range order and is highest in single crystals so that polymers start with a handicap. Thus poly-(*N*-vinylcarbazole), (PVK), has a low hole mobility (10^{-6} cm^2 V^{-1} s^{-1}) whereas the monomer model, *N*-isopropylcarbazole, as a single crystal has a high hole mobility (0.3 cm^2 V^{-1} s^{-1}).[1] Mobility is the parameter which has received least attention in studies of conducting polymers.

Charge carriers are most readily formed by activation of non-bonding or π-bonded electrons, and if they are delocalized in a conjugated system they form an internal conduction path of high mobility. Thus long conjugated systems

[1] D. L. Stockman, in 'Current Problems in Electrophotography', ed. W. F. Berg and K. Hauffe, de Gruyter, Berlin, 1972, p. 194.

form one class of organic conductors. Also π-bonded electrons give better intermolecular orbital overlap than σ-bonds. Hence we find that planar aromatic molecules which can stack like cards with an interplanar spacing no greater than that in graphite (0.335 nm), provide a conduction pathway normal to the molecular planes. Thus the second major class of organic conductors comprises the stacked planar π-electron systems.

3 Conjugated Molecules

In a polyene chain, —$(CH)_n$—, π-electron delocalization tends to make all the C—C bonds of equal length. By treating the system quantum mechanically as a particle in a box we find that the energy required to excite an electron from the ground to the first excited state is given by

$$E_A = 19(n + 1)/n^2$$

Thus as n increases the activation energy for carrier formation decreases and conductivity should increase with chain length. This is seen in a series of measurements on thiophenylene-ethylenes made by Kossmehle[2] (Figure 2); the slight
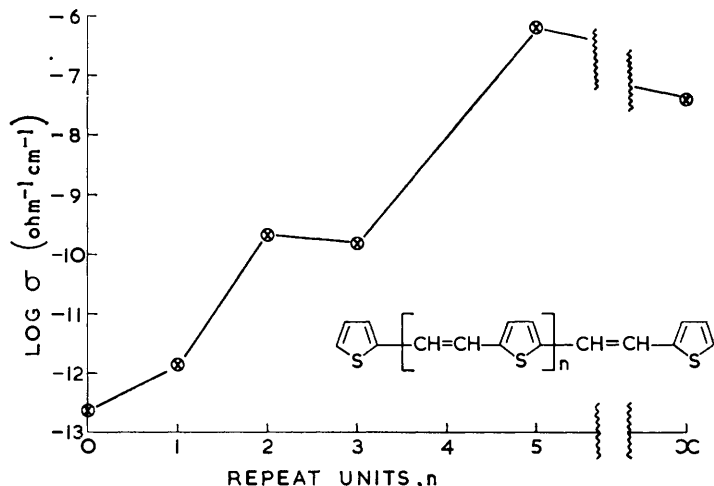

Figure 2 *Dependence of conductivity on the length of the conjugated system*

decrease in conductivity on passing from crystalline oligomer to partly crystalline polymer at $n > 5$ can also be seen.

For values of n typical of a polymer (*ca.* 1000), E_A becomes equal to the value of kT at room temperature (0.025 eV) and so the excited levels should become thermally populated. Thus we might expect metallic conduction in a

[2] M. Hartel, G. Kossmehl, G. Manecke, W. Willie, D. Wöhrle, and D. Zerpner, *Angew. Makromol. Chem.*, 1973, **29/30**, 307.

true polyene such as polyacetylene; however, it is found that only highly crystalline, stereoregular polyacetylenes show appreciable conductivity. The highest known conductivity ($\sigma = 10^{-3}$ ohm^{-1} cm^{-1}) is found in *trans*-polyacetylene which Shirakawa[3] made by Ziegler–Natta polymerization in a thin film. Polyphenylacetylene[4] is an insulator ($\sigma = 10^{-16}$ ohm^{-1} cm^{-1}) and the conductivity of polymethinimine, —$(CH=N)_n$—, recently made by the zinc chloride-catalysed polymerization of 1,3,5-triazine,[5] is little better ($\sigma = 1.3 \times 10^{-11}$ ohm^{-1} cm^{-1}). There are three reasons for this poor conductivity in polyenes: (i) the large intermolecular barrier; (ii) the bonds are not all equal in length but alternate. (This Jahn–Teller effect stabilizes the polymer but it restricts electron delocalization); (iii) rotation of the chain interrupts conjugation particularly where coplanarity of substituents is prevented by steric interaction, as in polyphenylacetylene.

Interrupted conjugation is overcome by locking the bonds in a planar polyacene structure as is found in pyropolymers and ultimately in graphite, but these are very intractable materials which must be fabricated before pyrolysis, as in the case of carbon fibres[6] which have a conductivity of $3 \times 10^{+2}$ ohm^{-1} cm^{-1}.

The polyacene quinone radical (PAQR) polymers are also very intractable substances. They are made by condensing pyromellitic anhydride with various aromatic compounds to form planar conjugated ladder polymers up to 5000 Å long (Figure 3). Pohl[7] found evidence of high intramolecular conductivity in the extraordinarily high dielectric permittivities shown by these polymers. Values of up to 300 000 were measured, compared with normal values of 2—7.
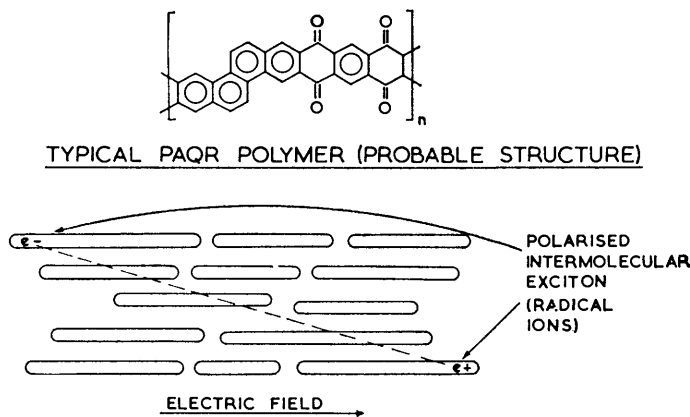

TYPICAL PAQR POLYMER (PROBABLE STRUCTURE)

Figure 3 *Ladder and layer structures of PAQR polymers, showing hyperelectronic polarizability*

[3] H. Shirakawa and S. Ikeda, *Polymer J.*, 1971, **2**, 231; Jap. Pat. 73 32 581.
[4] A. G. Hankin and A. M. North. *Trans. Faraday Soc.*, 1967, **63**, 1525.
[5] D. Wöhrle, *Makromol. Chem.*, 1974, **175**, 1751.
[6] R. W. Cahn and B. Harris, *Nature*, 1969, **221**, 132.
[7] R. D. Hartman and H. A. Pohl, *J. Polymer Sci., Part A*-1, *Polymer Chem.*, 1968, 6, 1135; H. A. Pohl, *J. Biol. Phys.*, 1974, **2**, 113.

The carriers slam to the ends of the molecules producing full polarization in weak fields. This effect Pohl calls 'hyperelectronic polarizability' and the uninterrupted conjugation he calls 'eka conjugation'. It is not certain that the bond length alternation in polyenes can be avoided by using planar polyacenes.[8]

Polyacetylenes are paramagnetic and Byrd *et al.*[9] showed that the conductivity of substituted polyphenylacetylenes is proportional to the electron spin concentration (Figure 4). Thus the carriers can be identified as unpaired electrons
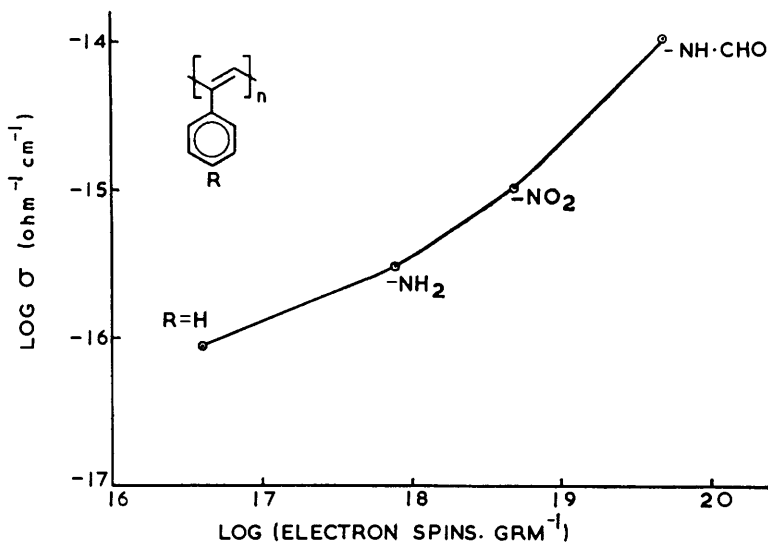

Figure 4 *Conductivity and unpaired electrons in polyphenylacetylenes*

which are probably formed by electron transfer from an excited triplet to a singlet molecule. The resulting intermolecular exciton ionizes to give radical-ions as the charge carriers, and it is probable that radical-ions are the carriers in the majority of organic molecular systems (*cf.* Figure 3).

$$^1A_0 + {}^3A_1 \longrightarrow A^{-\bullet} + A^{+\bullet}$$
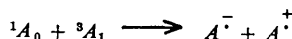
[8] M. R. Boon, *Theor. Chim. Acta*, 1971, **23**, 109.
[9] N. R. Byrd, F. K. Kleist, and D. N. Stamires, *J. Polymer Sci., Part A-2, Polymer Phys.*, 1972, **10**, 957.

In polyenes the first step towards carrier generation probably involves chain rotation to break double bonds,[10] and this can be prevented by locking the chain in a crystal lattice. There is one example of this in the polydiacetylenes made by Wegner[11] using solid-state polymerization in a single crystal (Figure 5). These
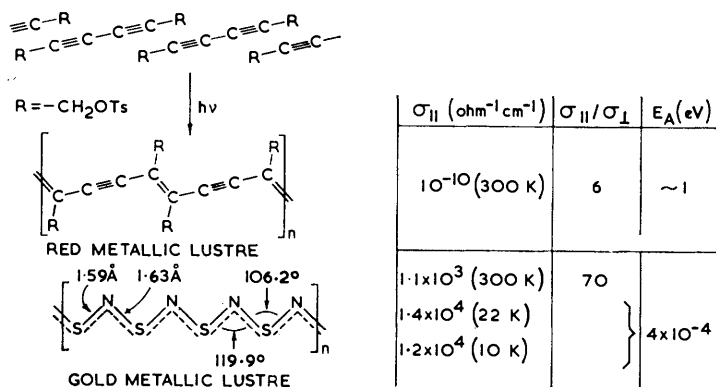

$\sigma_{\|}$ (ohm^{-1} cm^{-1})	$\sigma_{\|}/\sigma_{\perp}$	E_A(eV)
10^{-10} (300 K)	6	~1
1.1×10^3 (300 K)	70	
1.4×10^4 (22 K)		4×10^{-4}
1.2×10^4 (10 K)		

Figure 5 *Conductivities of polydiacetylene,*[11] *made by solid-state polymerization, and of poly(sulphur nitride)*[14]

polymer crystals are 1—15 cm long, have a metallic lustre, and are macroscopically free of defects. X-Ray analysis[12] shows that the polymer is planar and perfectly conjugated with bond alternation. Thus carriers cannot be readily formed by chain rotation. In agreement with this Bloor has now shown[13] that the polymer has no measurable electron spin, which also shows that the molecules are probably as long as the crystal and the intermolecular barrier to conduction must be negligible. So we see that charge carriers are probably generated by thermal excitation of π-electrons but that this is made difficult by bond alternation because the electrons are localized, thus explaining the high activation energy and low conductivity which probably occurs by hopping.

In spite of bond alternation, poly(sulphur nitride) as single crystals has metallic conductivity (Figure 5).[14] We shall return to this later.

To summarize, conjugated polymers can give fairly high conductivity but at the expense of poor mechnical properties, refractory behaviour, and dark colour. Fortunately an alternative electronic conduction pathway is found in the stacked planar π-electron systems. Charge-transfer complexes and certain radical-ion salts are of this type.

[10] G. M. Holob, P. Ehrlich, and R. D. Allendoerfer, *Macromolecules*, 1972, **5**, 569.
[11] W. Schermann and G. Wegner, *Makromol. Chem.*, 1974, **175**, 667; 1972, **154**, 35.
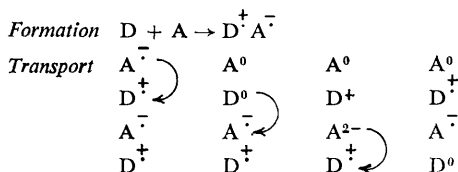[12] E. Hädicke, E. C. Mez, C. H. Krauch, G. Wegner, and J. Kaiser, *Angew. Chem. Internat. Edn.*, 1971, **10**, 266.
[13] D. Bloor, D. J. Ando, F. H. Preston, and G. C. Stevens, *Chem. Phys. Letters*, 1974, **24**, 407.
[14] C. H. Hsu and M. M. Labes, *J. Chim. phys.*, 1974, **61**, 4640; A. A. Bright *et al.*, *Phys. Rev. Letters*, 1975, **34**, 206.

4 Charge-transfer (CT) Complexes

Partial formation of radical-ions occurs in the donor–acceptor interaction leading to CT complexes which form rigid stacks, $\cdots$ DADADA $\cdots$, and these determine the mechanical properties of solid complexes. Conductivity is highly anisotropic and occurs by radical-ion disproportionation, as suggested by Eley.[15]

$$\textit{Formation} \quad D + A \rightarrow \overset{+}{D} \overset{-}{A}$$

$$\textit{Transport} \quad
\begin{array}{cccc}
\overset{-}{A} & A^0 & A^0 & A^0 \\
\overset{+}{D} & D^0 & D^+ & \overset{+}{D} \\
\overset{-}{A} & \overset{-}{A} & A^{2-} & \overset{-}{A} \\
\overset{+}{D} & \overset{+}{D} & \overset{+}{D} & D^0
\end{array}$$

Quite high conductivities are found, *e.g.* in the perylene–nickel maleonitriledithiolate complex.[16]

perylene   nickel maleonitriledithiolate
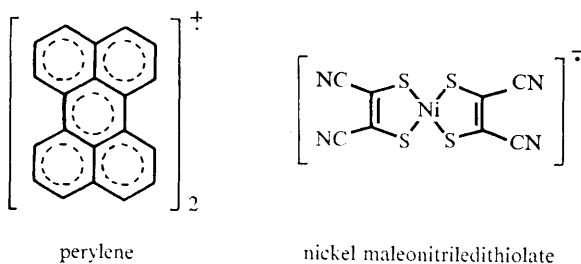
$$\sigma_{20\,°C} = 50 \text{ ohm}^{-1} \text{ cm}^{-1}$$

Many polymeric CT complexes have been made, usually with the donor species carried on a vinyl polymer. However, this often results in the conductivity being lower than that of the equivalent monomeric complex, *e.g.* in the phenothiazine–DDQ system (Figure 6).[17] Litt[18] attributes this to the small spacing of the donor repeat units and finds that by taking polyethyleneimine as the backbone the repeat spacing of methylmercaptoanisole donor units (0.635 nm) in the crystalline polymer is the same as the repeat distance of most CT complexes (0.64—0.68 nm). If 2,4,5,7-tetranitrofluorenone is used as acceptor, the conductivity of the polymeric complex is greater than that of the monomer by 10^3. Although the conductivities are low this is an important observation because it shows that the polymer can be tailored to give the correct geometry to facilitate sandwich stacking. The polymers are soluble and more tractable than the conjugated systems as the stiff rod-like stacks are plasticized by the flexible σ-bonded polymer matrix.

[15] D. D. Eley, *J. Polymer Sci., Part C, Symposia*, 1967, **17**, 78.
[16] L. Alcacer and A. H. Maki, *J. Phys. Chem.*, 1974, **78**, 215.
[17] R. Knoesel, B. Gebus, J.-P. Roth, and J. Parrod, *Bull. Soc. chim. France*, 1969, 294.
[18] M. H. Litt and J. W. Summers, *J. Polymer Sci., Polymer Chem.*, 1973, **11**, 1339.

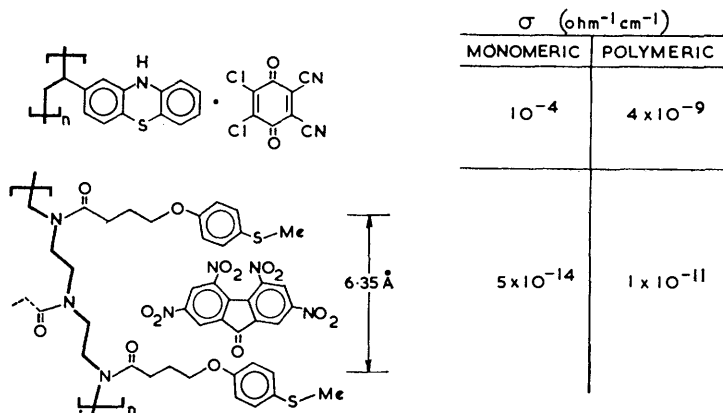|	σ $\left(ohm^{-1} cm^{-1}\right)$	
	MONOMERIC	POLYMERIC
	10^{-4}	4×10^{-9}
	5×10^{-14}	1×10^{-11}

Figure 6 *Polymeric charge-transfer complexes*

Complexes formed from polymeric donor and polymeric acceptor species, such as that based on PVK and shown in Figure 7, are claimed[19] to form films with conductivities as high as 10^{+3} ohm^{-1} cm^{-1}.
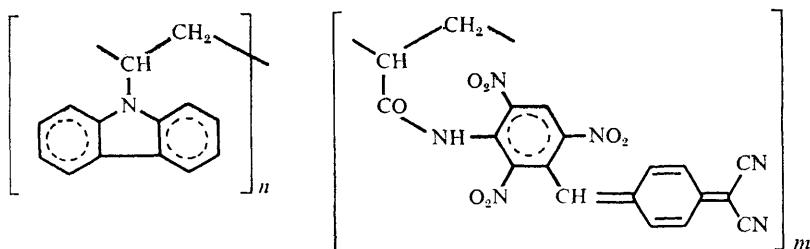
**Figure 7** *Charge-transfer complex of donor and accceptor polymers*

Generally these polymeric CT complexes are brittle materials, however. They are of value where mechanical properties are not important, as in the case of the poly-(2-vinylpyridine)–iodine complex which is used as a cathode in the miniature Li–I_2 primary cell made by Wilson Greatbatch Ltd[20] for implantable cardiac pacemakers (Figure 8). The complex serves a dual function as a source of iodine for the cell reaction
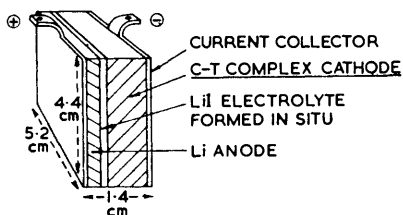
$$2Li + I_2 \rightarrow 2LiI$$
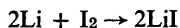
and as electronic conductor carrying the current to the collector. The conduc-

[19] H. Naarmann, Ger. Pat. 1 953 898, 1 953 899; *Angew. Chem.*, 1969, **81**, 871.
[20] A. A. Schneider, W. Greatbatch, and R. Mead, 9th International Power Sources Symposium, paper No. 30, 1974.

CELL REACTION $2 Li + I_2 \longrightarrow 2 LiI$
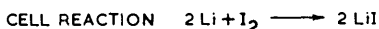
WT. 80 g
VOLTAGE 2·8V o.c.
CAPACITY 4 amp h
ENERGY DENSITY
    120 Wh · kg^{-1}

CURRENT COLLECTOR
C-T COMPLEX CATHODE
LiI ELECTROLYTE
FORMED IN SITU
Li ANODE

4·4 cm
5·2 cm
←—1·4—→ cm

C T COMPLEX $PVP:I_2 = 1:7-24$ (BY WT)

PVP = POLY (2-VINYLPYRIDINE)

$\overline{M}_n = 13\,000$

$\sigma = 10^{-3}$ ohm^{-1} cm^{-1}
AT 90-75% I_2

Figure 8 *Charge-transfer complex as cell electrode*

tivity of the complex is constant at 10^{-3} ohm^{-1} cm^{-1} as the iodine concentration falls from 90 to 75% on discharging the cell. This solid-state cell with the LiI electrolyte formed *in situ* has a very high energy density (120 w h kg^{-1}) compared with the best lead acid battery (30 w h kg^{-1}) and a service life of ten years. It illustrates the use of one commercially valuable conducting polymer.

5 Radical-ions

The classical radical-ion conductors are based on TCNQ, which forms the redox system shown in Figure 9. The system is characterized by the comproportionation constant K, which is a measure of the energy difference between the oxidation levels in terms of the redox potentials E_1 and E_2. TCNQ forms charge-transfer complexes and simple and complex salts such as those of quinoline. A complex salt usually has a higher conductivity than a simple salt, but simple salts can also have high conductivity if they are associated with a polarizable cation[21–23] as in N-methylphenazinium tetracyanoquinodimethanide, NMP-TCNQ (Figure 10) The TCNQ species form a homogeneous stack[24,25] and in NMP-TCNQ they are all equally spaced at 0.324 nm so that the unpaired electrons can delocalize into a conduction band to give metallic conductivity which falls as the temperature is increased. However, most simple salts are not band but hopping conductors,[26] in which the TCNQ species are unequally spaced as dimers on which the electrons are localized (0.324 nm between molecules in a dimer and 0.332 nm between dimers). This might be caused by steric

[21] A. F. Garito and A. J. Heeger, *Phys. Rev. (B)*, 1972, **5**, 952.
[22] J. R. Melby, *Canad. J. Chem.*, 1965, **43**, 1448.
[23] D. W. Bonniface, M. J. Braithwaite, D. D. Eley, R. G. Evans, R. Pethig, and M. R. Willis, *Discuss Faraday Soc.*, 1971, **51**, 131.
[24] C. J. Fritchie, *Acta Cryst.*, 1966, **20**, 892.
[25] H. Kobayashi, *Bull. Chem. Soc. Japan*, 1975, **48**, 1373.
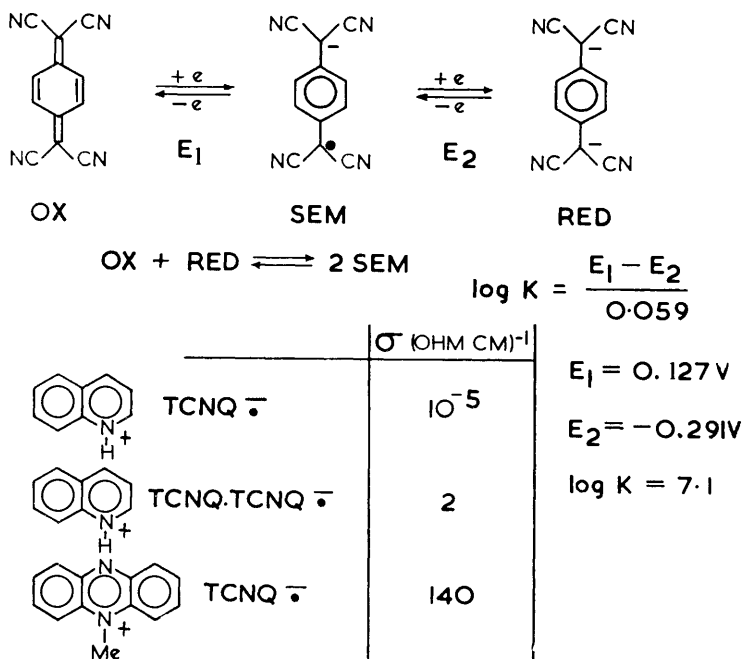[26] O. H. LeBlanc, jun., *J. Chem. Phys.*, 1965, **42**, 4307.

$$\log K = \frac{E_1 - E_2}{0.059}$$

		σ (OHM CM)$^{-1}$
	TCNQ $\bar{\cdot}$	10^{-5}
	TCNQ.TCNQ $\bar{\cdot}$	2
	TCNQ $\bar{\cdot}$	140

$E_1 = 0.127\,V$

$E_2 = -0.291V$

$\log K = 7.1$

Figure 9 *The 7,7,8,8-tetracyanoquinodimethane redox system*

3·24 (3·32) 3·24 Å

	σ (ohm^{-1} cm^{-1})
N-methylphenazinium^{+}TCNQ^{-}	1.4×10^{2}
N-ethylphenazinium^{+}TCNQ^{-}	10^{-9}
N-methylphenazinium^{+}(TCNQ$_{2}^{-}$)	7.1×10^{-1}
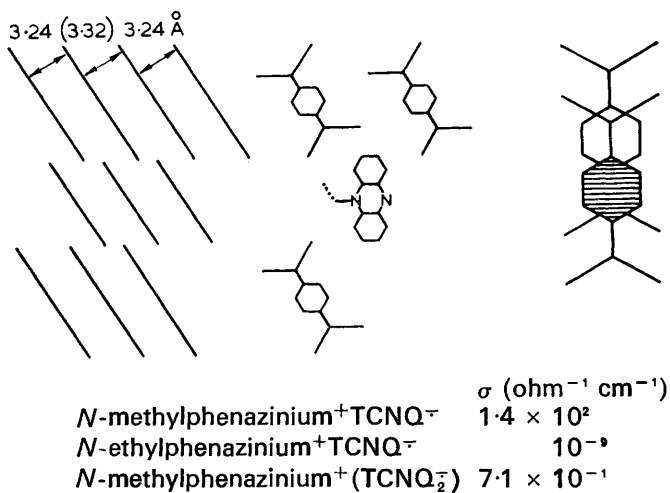
Figure 10 *Crystal structure of* N-*methylphenazinium TCNQ, and conductivities of this and related salts*

Simple salt   (diagram) ⟶ 0   2−   energy barrier

(TCNQ radical-ion   (neutral   (TNCQ
dimer)   TCNQ)   dianion)

Complex salt   (diagram) —→ 0   no energy barrier

(radical-ion)   (neutral   (neutral   (radical-ion)
mol.)   mol.)
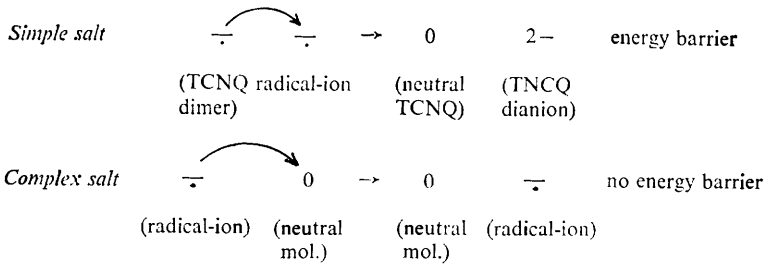
effects in the case of *N*-ethylphenazinium TCNQ simple salt which has 10^{11} times lower conductivity than NMP-TCNQ. Thus uniformity of the band system is destroyed and the salt is a semiconductor, although carrier mobilities might be quite high.[27]

The problem here is that for electrons to move along the stack, Coulomb forces have to be overcome in forming the dianion and so conduction is poor. If neutral TCNQ is added, however, it is not necessary to form a dianion and this is the reason why complex salts have a higher conductivity.[28] Sometimes this fails because electron transport from radical-anion to neutral TCNQ is hindered by the Coulombic attraction of the counter cation which is fixed in the solid alongside the radical-anion. However, this can be avoided by using lower concentrations of neutral TCNQ. These complex salts can be regarded as mixed valence conductors.

Although $NMP^+TCNQ^{\cdot-}$ has metallic conductivity it differs from metals because on cooling it becomes a semiconductor as shown in Figure 11. First
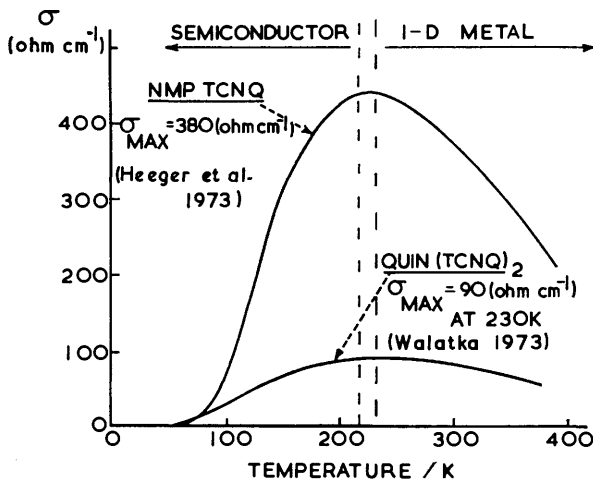

Figure 11 *The temperature dependence of the conductivity of 'metallic' TCNQ salts*

[27] G. J. Ashwell, D. D. Eley, S. C. Wallwork, and M. R. Willis, *Proc. Roy. Soc.*, 1975, A343, 461.
[28] V. Hadek, *Phys. Status Solidi*, 1968, 30, 275.

the conductivity reaches quite a high maximum (4×10^2 ohm^{-1} cm^{-1}) and then undergoes a transition to a semiconductor.[29] There are several theories explaining this transition.[30] It is possible that reorganization of the TCNQ stack is induced by asymmetry in the cation, and that the one-dimensional metal becomes a three-dimensional semiconductor because of radical-ion pairing.[31-33] This Peierls or metal–insulator transition, which is a form of the Jahn–Teller effect, results in a change in crystal structure.[34]

Many TCNQ salts of polymeric cations have been made and two examples are given in Figure 12.[35,36] The highest conductivities are *ca.* 10^{-2} ohm^{-1} cm^{-1}.
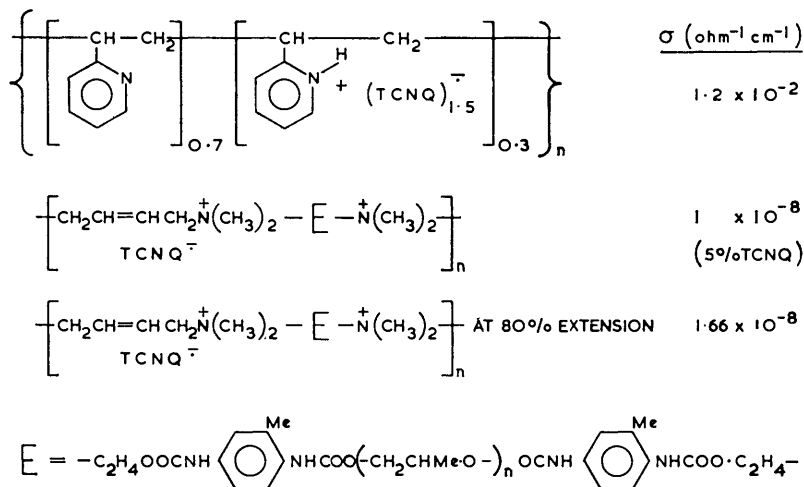

Figure 12 *Two examples of TCNQ salts of polymeric cations*

Mostly they are dark-coloured materials but owing to the plasticization of the rigid TCNQ stacks by the flexible σ-bonded polymer backbone they have better processability than the conjugated systems. Thus they are soluble in organic solvents and form brittle films. The conductivity of the TCNQ salts of poly-(2-vinylpyridine) seems to depend on polymer crystallinity[23] but not on tacticity.[35] We see here an example of maximum conductivity being achieved with a reduced concentration of neutral TCNQ^0. The elastomeric salt with 5% by weight of TCNQ has a low conductivity ($\sigma = 10^{-8}$ ohm^{-1} cm^{-1}) which nevertheless is

[29] M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *Phys. Rev. (B)*, 1974, **10**, 1298.
[30] L. L. van Zandt and J. M. Honig, *Ann. Rev. Mater. Sci.*, 1974, **4**, 191.
[31] M. J. Cohen, L. B. Coleman, A. F. Garito, and A. J. Heeger, *Phys. Rev. (B)*, 1974, **10**, 1298.
[32] P. A. Lee, T. M. Rice, and P. W. Anderson, *Phys. Rev. Letters*, 1973, **31**, 462.
[33] A. F. Garito and A. J. Heeger, *Accounts Chem. Res.*, 1974, **7**, 232.
[34] F. Denoyer, F. Comès, A. F. Garito, and A. J. Heeger, *Phys. Rev. Letters*, 1975, **35**, 445.
[35] E. P. Goodings, *Discuss. Faraday Soc.*, 1971, **51**, 157.
[36] A. M. Hermann, S. P. S. Yen, A. Rembaum, and R. F. Landel, *Polymer Letters*, 1971, **9**, 627.

much higher than that of the same polymer with 5% carbon black ($\sigma = 10^{-15}$ ohm^{-1} cm^{-1}). Moreover, the polymer retains its elasticity and on stretching by 80% the conductivity rises whereas that of the carbon composite is halved.

Unfortunately polymeric TCNQ salts gradually decompose in air and lose their conductivity.

6 Radical-cations

Radical-cations are also electronic conductors. Some of the earliest examples were the polyaniline radical ions[37] (Figure 13), which form stacked structures.[38]
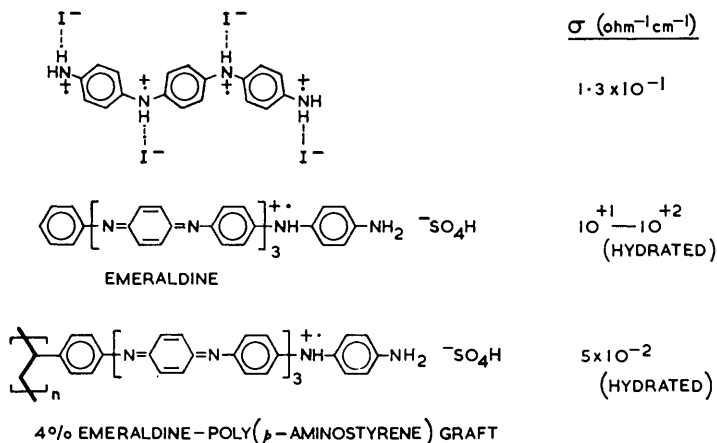

Figure 13 *Some polyaniline radical-cations, and their conductivities*

They are closely related to aniline black which, if carefully prepared as the linear emeraldine, has a high conductivity[39] but is a refractory substance. However, Labarre and Jozefowicz[40,41] grafted 4% emeraldine onto poly(p-aminostyrene) to give a polymer of conductivity 5×10^{-2} ohm^{-1} cm^{-1} which could be compaction moulded; attempts have been made to use it as a battery electrode. Here again the mixing of stiff molecules with flexible chains gives improved polymer properties.

[37] J. Honzl. K. Ulbert, V. Hadek, and M. Tlustakova, *Chem. Comm.*, 1965, 440.

[38] J. Huml, *Acta Cryst.*, 1967, **22**, 29.

[39] M. Jozefowicz, L. T. Yu, G. Belorgey, and R. Buvet, *J. Polymer Sci.. Part C, Symposia*, 1967. **16**, 2943; R. Buvet, M. Guillon, and L. T. Yu, *Ion Exchange Solvent Extraction*, 1973. **4**, 181; M. Jozefowicz. L. T. Yu. J. Perichon, and R. Buvet, *J. Polymer Sci.*, *Part C*, *Symposia*. 1969. **22**, 1187; M Doriomedoff, F. H. Cristofini, R. De Surville, M. Jozefowicz, L. T. Yu, and R. Buvet, *J. Chim. phys.*, 1971. **68**, 1055.

[40] D. Labarre and M. Jozefowicz. *Compt. rend.*, 1969, **269**, C, 964.

[41] X. Gerbaux, A. Hadni, M. Heider, M. Jozefowicz, D. Labarre, and J. Néel, *J. Chim. phys.*, 1970, **67**, 684.

Heterocyclic radical-cations which are even polyenes, like TCNQ, are particularly stable and form the fulcrum of the violene redox systems[42] (Figure 14) in
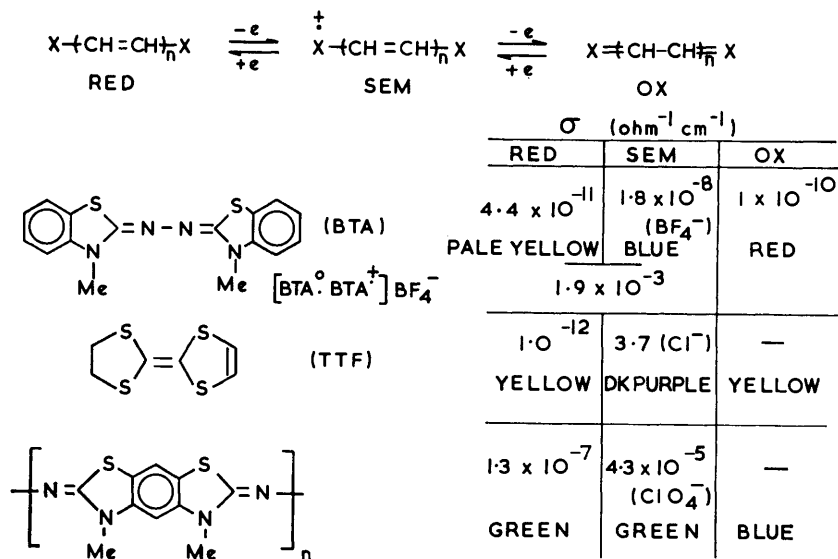

Figure 14 *The violene redox system*

which the reduced form is usually much paler in colour than the radical-cation. The radical-cation of 1,4,5,8-tetrathiafulvalene (TTF) has a much higher conductivity than the neutral material. The radical-cation of benzothiazolidin-oneazine (BTA·+) has been incorporated by Manecke[43] into a polymer which probably combines both radical-ion and conjugated-chain type conductor classes, as both oxidation levels have higher conductivies than the corresponding monomers. Here, as there are no flexible chains present, the stiff molecules give a refractory solid.

The complex salt $BTA^0 BTA \cdot^+ BF_4^-$ has a much higher conductivity (10^{-3} ohm^{-1} cm^{-1}) than either component, as would be expected. But the effect of traces (6 p.p.m.) of radical-cation on the conductivity of neutral BTA is remarkable in increasing the conductivity by 10^4 or 10^5 (Figure 15).[44] This is analogous to the doping of Ge by In to give a *p*-type semiconductor and renders doubtful many recorded values of conductivity in radical-ion systems.

Although polymeric TCNQ salts partly solve the problem of refractory

[42] S. Hünig, *Pure Appl. Chem.*, 1967, **15**, 109.
[43] G. Manecke and J. Kautz, *Makromol. Chem.*, 1973, **172**, 1.
[44] W. A. Barlow, G. R. Davies, E. P. Goodings, R. L. Hand, G. Owen, and M. Rhodes, 4th International Symposium on Organic Solid State, Bordeaux, July, 1975; to be published.
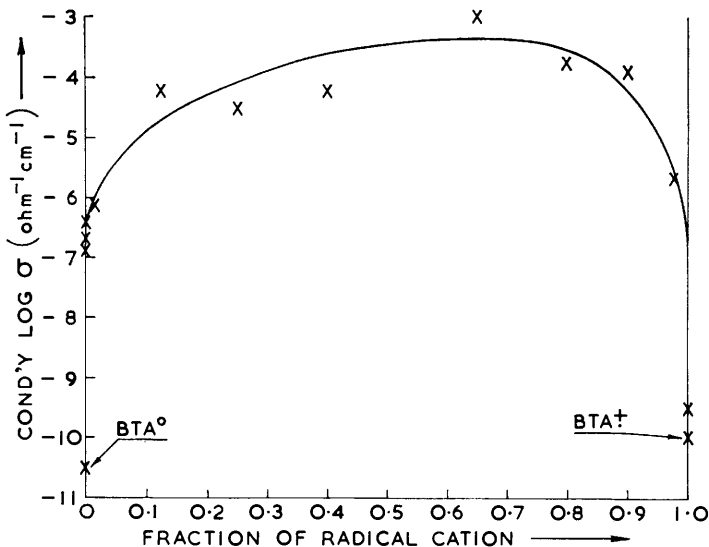
Figure 15 *The effect on conductivity of doping in the benzothiazolidinoneazine system*

properties in organic conductors they are strongly coloured and sensitive to air. The use of lightly coloured neutral violenes doped with traces of radical-cation means that a solution to these problems is in sight.

7 Photoconduction
Radical-ions can also be generated by photoprocesses and this leads to photo-conduction. It is the most complex aspect of conduction but must be mentioned in this survey as it is the basis of the electrophotographic industry annually worth some £600M.[45]

In xerography (Carlson,[46] 1954) a photoconductor coated on a metal drum is negatively charged in the dark by a corona discharge (Figure 16). The image to be copied is projected onto the photoconductor, thereby discharging the light areas. Black positively charged toner powder coated with resin is sprayed onto the latent image where it is held and subsequently transferred to negatively charged paper. The image is finally fixed by heating to sinter the resin.

The photoconductor formerly used was As_2Se_3 but this is difficult to manipulate as it is applied by vacuum sublimation and is brittle. It is now being replaced by materials based on poly-(N-vinylcarbazole) (PVK)[47] which is a good dark insulator whose photoconductive properties were discovered in 1957 by Hoegl.[48]

[45] C. H. L. Goodman, in 'Electronic and Structural Properties of Amorphous Semi-conductors', ed. P. G. LeComber and J. Mort, Academic Press, 1973, p. 549.
[46] A. A. Newmann, *Brit. J. Photogr.*, 1964, Sept. 25, 784.
[47] G. Weiser. *J. Appl. Phys.*, 1972, **43**, 5028.
[48] H. Hoegl, O. Süs, and W. Neugebauer, Ger. Pat., 1 111 935; 1 068 115.
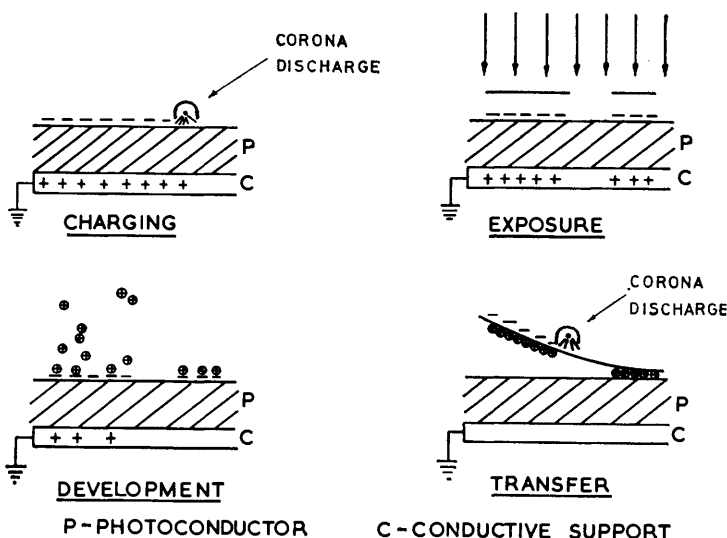
Figure 16 *The stages in the electrophotographic process*

It absorbs u.v. light (360 nm) forming an exciton state which ionizes in an electric field[49] (Figure 17), and the electron is stabilized in trapping levels of low potential (carbazole dimer units)[50] leaving only the radical-cations, PVK·+, to
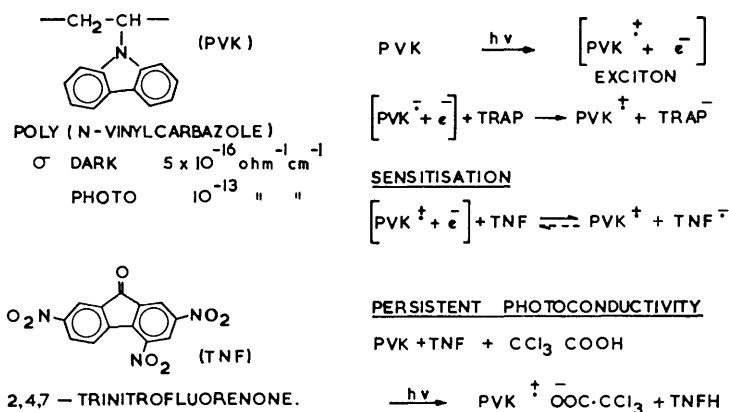

Figure 17 *The photoconductivity of poly*(N-*vinylcarbazole*)

[49] K. Kato, T. Nogami, M. Yokoyama, and H. Mikawa, *Chem. Letters*, 1974, 1097; R. R. Chance and C. L. Braun, *J. Chem. Phys.*, 1973, 59, 2269.

[50] H. Bauser and W. Klöpffer, *Chem. Phys. Letters*, 1970, 7, 137; H. Meier, W. Albrecht, and U. Tschirwitz. in 'Current Problems in Electrophotography', ed. W. F. Berg and K. Hauffe, de Gruyter, Berlin, 1972, p. 163.

act as charge carriers ($\sigma_{360nm} = 10^{-13}$ ohm^{-1} cm^{-1}). Indirect evidence for the formation of radical-cations comes from studies of photoconduction in anthracene[51] and also the increase in photoconductivity of various compounds on introducing substituents which reduce the ionization potential.[52] In visible light PVK remains an insulator ($\sigma_{550nm} = 10^{-16}$ ohm^{-1} cm^{-1}) but can be sensitized with an electron acceptor, 2,4,7-trinitrofluorenone (TNF), which by forming charge-transfer states shifts the absorption into the visible[53] and renders it photoconductive ($\sigma_{550nm} = 10^{-13}$ ohm^{-1} cm^{-1}). PVK is solely a hole conductor but the TNF creates electron carriers and the mobility increases. The radical-anion TNF·$^{-}$ contributes to the conductivity, and the amorphous nature of PVK is important in giving the chain the flexibility necessary to accommodate the PVK–TNF sandwich complex in the polymer matrix.[54] Support for this mechanism comes from Williams,[55] who found that addition of trichloroacetic acid protonated the radical-anion thus preventing recombination with the radical cation, PVK·$^{+}$. The salt PVK·$^{+}$ $^{-}$OOCCCl$_3$ is fairly stable and so results in persistent dark conductivity of several days duration.

Thus PVK is another commercially important conducting polymer and for this reason its charge transport properties have been studied in greater detail than those of any other polymer.

8 Organometallic Polymers

The introduction of metal atoms into a polymer can increase the conductivity. This usually arises from (i) improved intermolecular orbital overlap due to the more diffuse metal d-orbitals and (ii) extension of the intramolecular conduction path by conjugation of the d-orbitals with the π-electron system of the polymer so that the path passes through the metal atoms even if they form the sole links in the polymer chain. The effect of chelating metal ions onto a conjugated polymer is seen in the structure (1), which has a higher conductivity (1.4 $\times$ 10^{-10} ohm^{-1} cm^{-1}) than that of the unmetallized form (4.5 $\times$ 10^{-13} ohm^{-1} cm^{-1}).[2]
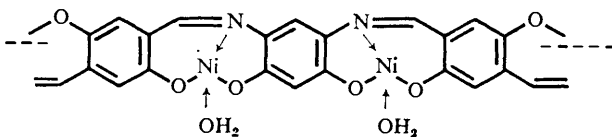
(1)

If the polymer chain is not conjugated then improved conductivity is still possible because with a transition metal a mixed-valence state system can

[51] B. J. Mulder and J. de Jonge, *Solid State Comm.*, 1967, **5**, 203.

[52] J. Rochlitz, *Chem. Ztg.*, 1972, 96, 561.

[53] H. Hoegl. G. Barchietto, and D. Tar, *Photochem. and Photobiol.*, 1972, 16, 335; M. Lardon, E. Lell-Doller, and J. W. Weigl, *Mol. Crystals*, 1967, 2, 241.

[54] W. Klöpffer. *J. Chem. Phys.*, 1969. **50**, 2337.

[55] D. J. Williams, G. Pfister, and M. Abkowitz, *Tappi*, 1973, **56**, 129.

transport electrons by redox behaviour. This is illustrated by the ferrocene-ferricenium polymers (Figure 18), which conduct by metal to metal hopping with-
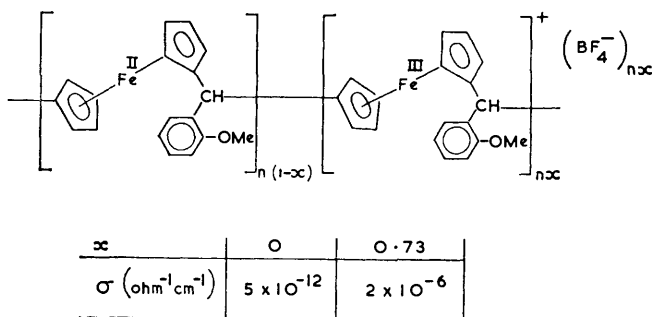

x	0	$0 \cdot 73$
$\sigma \left(ohm^{-1} cm^{-1} \right)$	5×10^{-12}	2×10^{-6}

Figure 18 *Mixed valence ferrocene–ferricinium polymer*

out participation by the organic framework.[56] Although the unoxidized ferrocene polymer is practically an insulator, the partly oxidized form has a conductivity of 10^{-6} ohm^{-1} cm^{-1}. Moreover, Pittman *et al.*[57] have now shown that a doping effect is observed analogous to, but less marked than, that which has been found with radical-ions. The addition of 5% of the ferricenium (Fe^{III}) form to the reduced (Fe^{II}) form of both unconjugated and conjugated ferrocene polymers

poly(ferrocenylene)   poly(ethynylferrocene)   poly-(3-vinylbisfulvalenedi-iron)
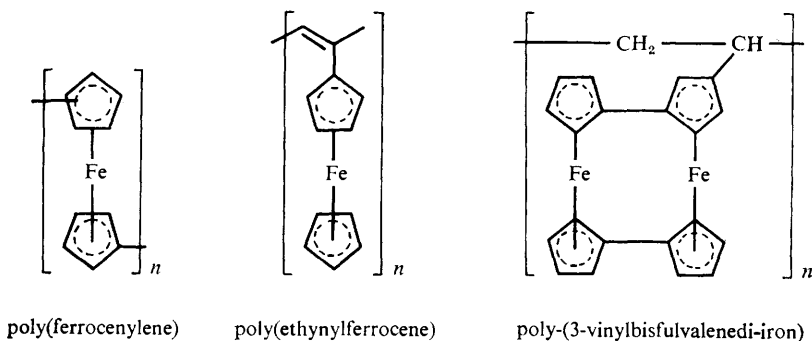
increases the conductivity by about 10^3. A maximum increase of 10^7 to 10^8 fold is reached in poly(ferrocenylene) with 35—65% Fe^{III} using tri-iodide as counter anion ($\sigma = 10^{-7}$ ohm^{-1} cm^{-1}). The hopping mode dominates the conductivity even when a conjugated system is present as in poly(ethynylferrocene). By super-imposing the TCNQ radical-ion system even higher conductivities can be

[56] D. O. Cowan, J. Park, C. U. Pittman, Y. Sasaki, T. Mukherjee, and N. A. Diamond, *J. Amer. Chem. Soc.*, 1972, **94**, 5110.
[57] C. U. Pittman, Y. Sasaki, and T. K. Mukherjee, *Chem. Letters*, 1975, 383.

realized. Poly-(3-vinylbisfulvalenedi-iron) with 71% of the iron in the ferricenium form as the TCNQ (probably complex) salt has a conductivity of 9×10^{-3} ohm^{-1} cm^{-1}.[58] This is a rather refractory black powder but attempts to improve the polymer properties by copolymerization with 72 mol % styrene reduced the conductivity to 2.5×10^{-5} ohm^{-1} cm^{-1}. Some of these polymers are soluble but as usual no mechanical properties have been reported.

In the hopping mixed-valence systems the metal atoms have a different geometry according to their oxidation state and any constraints on a change in geometry could lower the conductivity.[59] It is interesting that those biological conducting polymers which transport electrons through metalloproteins with metal sites 2.5—5.0 nm apart avoid this problem because the geometry of the metal complex is a compromise between those of the reduced and oxidized states.[60,61]

The metal is more effective if it forms square-planar complexes with conjugated ligands. Thus the Cu^{II} complex of 1,5-diformyl-2,6-dihydroxynaphthalene dioxime (2), although a refractory solid, has a conductivity of 4×10^{-5} ohm^{-1} cm^{-1}.[62] If a mixture of transition-metal ions is used in this type of polymeric complex the conductivity can be increased.[63]
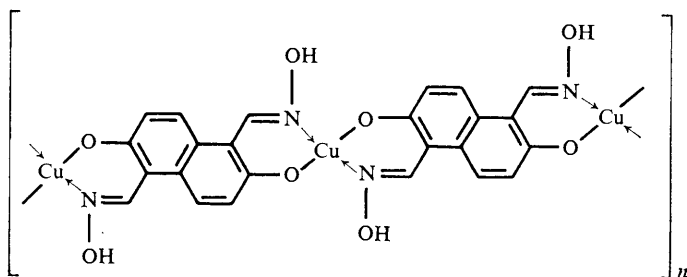
(2)

In these planar complexes the molecules are usually linked by metal d-orbital bonds perpendicular to the plane, and thus the carrier mobility tends to increase. An excellent example of this is copper phthalocyanine, which has the highest mobility of any organic compound (75 cm^2 V^{-1} s^{-1})[64] although the conductivity is low (*ca.* 10^{-14} ohm^{-1} cm^{-1}).[65,66] Here the copper d_{z^2} orbitals overlap with the azamethine nitrogen $3d$ orbitals of the neighbouring molecules with an inter-

[58] C. U. Pittman and B. Surynarayanan, *J. Amer. Chem. Soc.*, 1974, **96**, 7916.
[59] D. O. Cowan, C. LeVanda, J. Park, and F. Kaufman, *Accounts Chem. Res.*, 1973, **6**, 1.
[60] R. J. P. Williams, *Biochem. Soc. Trans.*, 1973, **1**, 1.
[61] J. R. McKellar, J. A. Weightman, and R. J. P. Williams, *Discuss. Faraday Soc.*, 1971, **51**, 176.
[62] M. J. S. Dewar and A. M. Talati, *J. Amer. Chem. Soc.*, 1963, **85**, 1874; 1964, **86**, 1592.
[63] Y. Akiyama and H. Mizutani, *J. Phys. Soc. Japan*, 1969, **26**, 1128.
[64] G. H. Heilmeier and S. E. Harrison, *Phys. Rev.*, 1963, **132**, 2010.
[65] B. S. Wildi and J. E. Katon, *J. Polymer Sci., Part A2, Polymer Phys.*, 1964, 4709.
[66] C. Hamann and H. Schmidt, *Plaste u Kaut.*, 1969, **16**, 85.

planar distance of 0.338 nm.[64] On extending the conjugation by polymerization the conductivity is increased by a factor of 10^{12} to 5×10^{-2} ohm^{-1} cm^{-1} in copper polyphthalocyanine (Figure 19) which is made from pyromellitonitrile.[65,67]
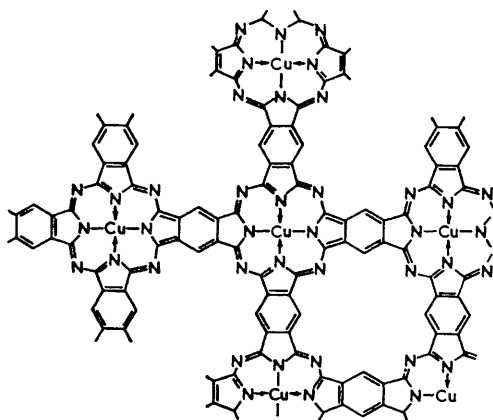

Figure 19 *Copper polyphthalocyanine*

However, the mobility then falls to 10 cm^2 V^{-1} s^{-1}.[67] As might be expected copper polyphthalocyanine is an insoluble, infusible solid and the only effect of introducing ether or sulphide links appears to be a reduction in conductivity to 10^{-6}—10^{-11} ohm^{-1} cm^{-1}.[66]

Polymerization can also occur through the metal atom[66,68] but in poly-{oxy(phthalocyanine)silandiyl} (3) the resultant separation of the phthalocyanine planes by oxy-groups, although resulting in lower conductivity (6×10^{-7} ohm^{-1} cm^{-1}) does not give an insulator. Substitution of the oxy by the bigger —OC$_2$H$_4$O— group further reduces the conductivity to 3.7×10^{-11} ohm^{-1} cm^{-1}.
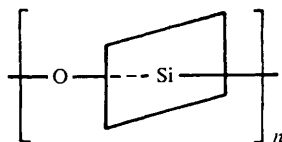
(3)

Polymeric porphyrin-like metal complexes have been made from various tetranitriles and have conductivities of up to 10^{-1} ohm^{-1} cm^{-1}.[2,65] Although

[67] A. Epstein and B. S. Wildi, *J. Chem. Phys.*, 1960, **32**, 324.
[68] G. Meyer and D. Wöhrle, *Makromol. Chem.*, 1974, **175**, 714.

they have high thermal stability and can either be fabricated by forming *in situ* on heating a mixture of metal and nitrile or be deposited as a film on the metal[69] they have found no technical application so far.

The copper polyphthalocyanine type structure exemplifies both conjugated and stacked planar conduction systems. Transition-metal complexes with planar ligand systems also can form a mixed-valence structure which is different from the ferrocene–ferricenium system where the metal atoms are in integral oxidation states. These are the Krogmann salts[70,71] which are square-planar complexes of d^8 transition-metal ions such as those of Pt and Ir. In potassium cyanoplatinate (Figure 20) the weak d_σ–d_σ metal–metal bonds are strengthened by removing
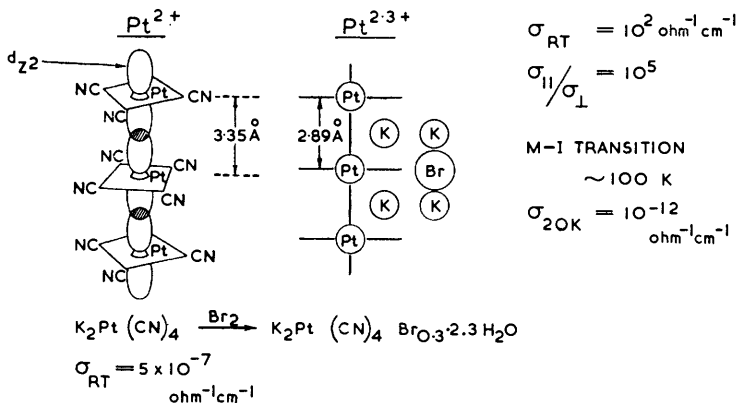

Figure 20 *Potassium cyanoplatinate and its bromine oxidation to a fractional oxidation level*

one third of the electrons from the d_{z^2} antibonding orbitals by bromine oxidation. This results in a fractional oxidation level of 2.3 giving the compound $K_2Pt(CN)_4$ $Br_{0.3}$, $2.3H_2O$ (KCP), with equivalent Pt atoms. In effect this is a polymerization as the decrease in interplanar distance from 0.335 to 0.289 nm gives a bonded chain of metal atoms which now forms a conduction band 5/6 full. The conductivity, which increases on oxidation from 10^{-7} to 10^{+2} ohm^{-1} cm^{-1}, is metallic and highly anisotropic, being 10^5 times greater parallel to than perpendicular to the metal–metal chain. Thus KCP is a one-dimensional metal and like NMP-TCNQ it shows a metal–insulator transition at *ca.* 100 K below which the conductivity is very low. In this case the phase change[72] might be due to an asymmetric

[69] S. D. Levina, K. P. Labanova, A. A. Berlin, and A. I. Sherle, *Doklady Akad. Nauk. S.S.S.R.*, 1962, **145**, 602.
[70] K. Krogmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 35.
[71] M. J. Minot and J. H. Perlstein, *Phys. Rev. Letters*, 1971, **26**, 371.
[72] R. Comès, M. Lambert, H. Launois, and H. R. Zeller, *Phys. Rev. (B)*, 1973, **8**, 571; *Phys. Status Solidi (B)*, 1973, **58**, 587.

location of the potassium or bromide ions in the lattice.[73] They are very brittle solids.

Few organometallic polymers with covalent metal–metal bonds have been described. A unique example is the homoatomic ladder polymer bis{*catena*-polymethylarsenic} (4). It forms a purple crystalline insoluble solid which can be sublimed to give thin films. It appears to be a band-type conductor with a high mobility estimated to be 1 cm^2 V^{-1} s^{-1}. With an energy gap of 1.2 eV the conductivity is low (5 × 10^{-10} ohm^{-1} cm^{-1}) but increases in photoconduction.[74]
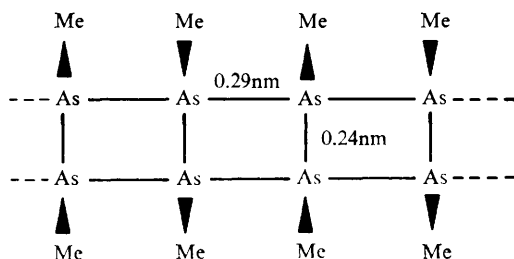
(4)

The ladders are coplanar, forming a two-dimensional metallic arsenic species, and the polymer probably represents the closest known approach to the structure of an inorganic semiconductor. Although its electrical properties probably could be adjusted by doping, its mechanical properties would restrict its use to specialized applications. Indeed this is true of all the organometallic polymers. It is possible that a superconductor might be found in the organometallic class but otherwise the most likely outlet for these polymers would be as photoconductors in optoelectronic devices.

We see then that organometallic polymers include examples of both conjugated and stacked planar systems. The mixed-valence polymers find analogies in the semiconducting radical-ion salts and the Krogmann-type structures fall in the same class as the metallic conductor radical-ion systems. As with their purely organic counterparts, the organometallic polymers must have better mechanical properties before they become generally useful as conductors.

We will now discuss the use of both conjugated and stacked planar systems in the search for room temperature superconduction.

9 Superconduction

Metals such as lead superconduct at around 4 K because the conduction

[73] J. H. Perlstein, M. J. Minot, and V. Walatka, *Mater. Res. Bull.*, 1972, **7**, 309; J. M. Williams, S. W. Petersen, J. L. Petersen, H. M. Gerdes, and F. K. Ross, *Chem. Eng. News*, 1974, Aug. 19, 23.

[74] A. L. Rheingold, J. E. Lewis, and J. M. Bellama, *Inorg. Chem.*, 1973, **12**, 2845; J. E. Lewis and M. Edris, *Bull. Amer. Phys. Soc.*, 1975, **20**, 695; *Phys. Rev. (B)*, 1975, **11**, 4033.

electrons pair together in an attractive potential developed by the polarization of the positive metal ions (the electron–phonon mechanism). The resistivity is then zero but above a critical temperature, T_c, conduction reverts to that of an ordinary metal. The value of T_c is inversely proportional to the square root of the atomic mass of the metal and the highest value is likely to be 25 K. A value of 23.2 K has been recorded for Nb_3Ge.[75] Hence sophisticated refrigeration techniques will always be necessary in order to use these electron–phonon superconductors.

In 1964, Little[76] suggested that the attractive potential needed to pair the conduction electrons should be created by polarizing a system of auxiliary electrons rather than heavy-atom cores, and because of the low electron mass he predicted transition temperatures above 1000 K. He proposed using a polyene chain as the conduction path (Figure 21) and cyanine dye side-groups
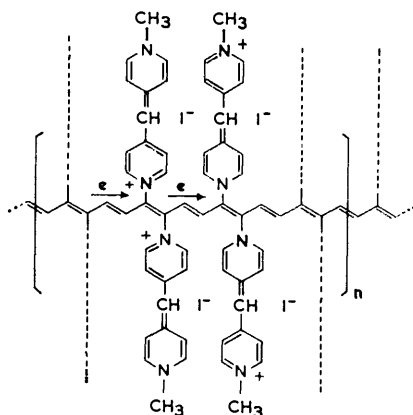

Figure 21 *Typical model for an organic superconductor according to Little*[76]

with their highly polarizable auxiliary electrons to provide the polarization 'well', thus giving the famous Little superconducting polymer.

So far no-one has made this polymer, the nearest approach being that of Liepins[77] who used the conjugated polymaleonitrile backbone (5), but none of his structures showed superconductivity.
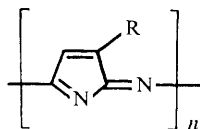
(5) R — dye side-group

[75] L. R. Testardi, J. H. Wernick, and W. A. Royer, *Solid State Comm.*, 1974, 15, 1.
[76] W. A. Little, *Phys. Rev. (A)*, 1964, **134**, 1416.
[77] R. Liepins, C. Walker, H. A. Fairbank, P. Lawless, and C. Moeller, *Amer. Chem. Soc., Polymer Preprints*, 1970, **11**, Sept., 1048.

As an alternative to the conjugated system a stacked planar one-dimensional metal might function as the conducting spine, and so TCNQ salts of cyanine dyes have been studied but without success.[78] One obstacle is the metal–insulator transition which converts the metallic TCNQ conductor into an insulator on cooling down in the search for superconductivity. In $NMP^+TCNQ^{\cdot-}$ the transition has been blamed on the asymmetric cation and so the symmetrical small and highly polarizable tetrathiafulvalene radical cation (TTF) was examined (Heeger[79]). The salt $TTF^{\cdot+} TCNQ^{\cdot-}$ as single crystals showed (Figure 22) highly
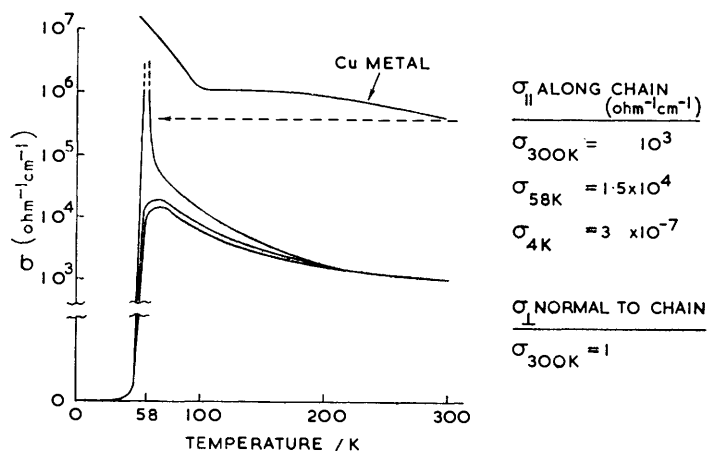

**Figure 22** *Superconducting fluctuations in* $TTF^{\cdot+}TCNQ^{\cdot-}$

anisotropic metallic conductivity which increased from 10^3 at room temperature to a maximum of 1.5×10^4 at 66 K, the highest value recorded for an organic material. Then at 58 K it underwent a metal–insulator transition. However, the transition temperature had been lowered considerably compared with NMP-TCNQ (220 K). But the remarkable feature was that in a few samples, just before the transition there was an enormous increase in conductivity to above 10^6 ohm^{-1} cm^{-1}. This exceeds the conductivity of copper at room temperature and has been attributed to fluctuations that herald superconductivity. Heeger[79] thinks that electron pairing is occurring by the usual phonon mechanism and not according to Little's mechanism, but the system is unstable and on further cooling the peak collapses. Moreover, the samples are not reproducible and no other worker has observed these giant conductivity peaks.

True superconduction might be realized if the metallic state could be stabilized

[78] J. H. Lupinski, K. R. Walter, and L. H. Vogt, *Mol. Crystals*, 1967, **3**, 241; E. B. Yagubsky, M. L. Khidekel, I. F. Shchegoleyev, L. I. Buravov, R. B. Lynbovsky, and V. B. Strynkov, *Zhur. obshchei Khim.*, 1968, **38**, 992.
[79] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J Heeger, *Solid State Comm.*, 1973, **12**, 1125.

above the Peierls transition. It has now been found that the non-planar hexa-methylene-1,4,5,8-tetraselenafulvalene (HMTSF) (6) forms a CT salt with TCNQ (HMTSF-TCNQ, σ_{300} $_\mathrm{K}$ = 2 × 10^3 ohm^{-1} cm^{-1}) which does not undergo a metal–insulator transition.[80] But although it remains metallic down to 0.045 K neither giant peaks nor superconduction were found.
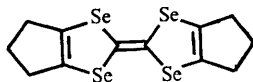
(6)

Moreover, although it has been shown that in the solid state TTF-TCNQ is essentially a CT salt, consisting of segregated stacks of TTF·$^+$ and TCNQ·$^-$ radical-ions as in Na$^+$ TCNQ·$^-$ and NMP$^+$ TCNQ·$^-$ where electron transfer is complete,[81,84] the precise degree of electron transfer is not known. It is possible[82] that the TTF and TCNQ molecules, respectively, are not all equivalent and both neutral and ionic (closed and open shell) forms contribute to the structure. Recent work[82,83] suggests that small amounts of neutral TTF^0 and TCNQ^0 are present and consequently they could function as dopants in the radical-ion stacks.

Hence TTF-TCNQ probably behaves as two sets of doped conducting chains with the expected high conductivity, and the lack of reproducible behaviour could be due to the variable composition sometimes found on recrystallizing a CT complex. In fact, the giant peaks might be unrelated to superconduction and the use of stacked planar systems might be the wrong approach. It might be easier to achieve long-range order in a conjugated polyacene system so that Little could be right and we shall have to face the problem of making his model.

To support this view comes a very recent report from Greene *et al* [85] at IBM that they have found superconduction in poly(sulphur nitride). The polymer does

[80] A. N. Bloch, D. O Cowan, K. Bechgaard, R. E. Pyle, R. H. Banks, and T. O. Poehler, *Phys. Rev. Letters*, 1975, **34**, 1561.

[81] L. B. Coleman, J. A. Cohen, A. F. Garito, and A. J. Heeger, *Phys. Rev. (B)*, 1973, **7**, 2122; T. E. Phillips, T. J. Kistenmaker, J. P. Ferraris, and D. O. Cowan, *J.C.S. Chem. Comm.*, 1973, 471; J. C. Scott, A. F. Garito, and A. J. Heeger, *Phys. Rev. (B)*, 1974, **10**, 3131.

[82] Y. Tomkiewiez, J. B. Torrance, B. A. Scott, and D. C. Green, *J. Chem. Phys.*, 1974, **60**, 5111; W. D. Grobman, R. A. Pollak, D. E. Eastman, E. T. Maas, jun., and B. A. Scott, *Phys. Rev. Letters*, 1974, **32**, 534.

[83] P. Coppens, *Phys. Rev. Letters*, 1975, **35**, 98, F. Denoyer, F. Comès, A. F. Garito, and A. J. Heeger, *Phys. Rev. Letters*, 1975, **35**, 445; W. T. Wozniak, G. Depasquali, M. V. Klein, R. L. Sweany, and T. L. Brown, *Chem. Phys. Letters*, 1975, **33**, 33.

[84] P. Nielsen, D. J. Sandman, and A. J. Epstein, *Solid State Comm.*, 1975, **17**, 1067; B. H. Schechtman, S. F. Lin, and W. E. Spicer, *Phys. Rev. Letters*, 1975, **34**, 667; P. Nielsen, A. J. Epstein, and D. J. Sandman, *Solid State Comm.*, 1974, **15**, 53; A. J. Epstein, N. O. Lipari, P. Nielsen, and D. J. Sandman, *Phys. Rev. Letters*, 1975, **34**, 914; A. J. Epstein, N. O. Lipari, D. J. Sandman, and P. Nielsen, *Phys. Rev. (B)*, in the press.

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not show a metal–insulator transition and remains metallic at low temperatures (Figure 23) with a conductivity of 5000 ohm^{-1} cm^{-1} at 1 K. All resistance is
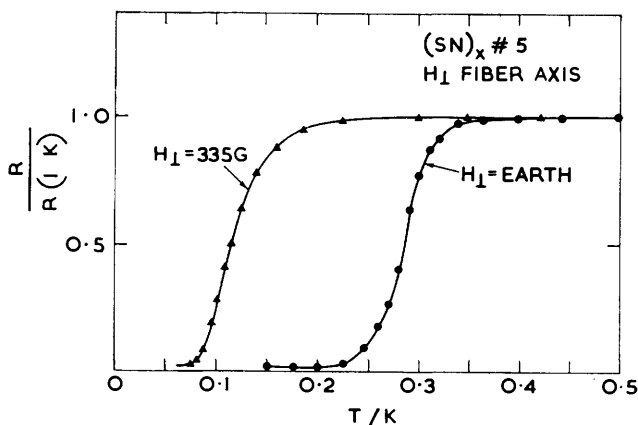

Figure 23 *Superconductivity in poly(sulphur nitride)*
(Reproduced by permission from *Phys. Rev. Letters*, 1975, **34**, 557.)

lost at 0.26 K and this is proved to be superconduction by the depression of the transition temperature to 0.1 K by a magnetic field of 335 G (the Meissner effect[86]).

This then is the first superconducting polymer but it is inorganic and far from being a room-temperature superconductor. It is a crystalline fibrous material but fully oriented epitaxial thin films of the polymer have been prepared on polyethylene and poly(ethylene terephthalate) which should make the material more easily adaptable to useful applications.[87]

We have seen that certain organometallic polymers can provide a conducting spine and much of the intense interest in KCP and related Krogmann salts has been in search of superconductivity. Indeed platinum complexes of the mixed-valence type bearing cyanine dye ligands have been made but neither these nor truly covalent catenated heteroatomic organometallic systems (Figure 24) have shown superconductivity[88] possibly because steric repulsion of the ligands reduces the intermetallic interaction and so reduces carrier mobility.[89]

Biological polymers must also be considered. They are well known as semi-

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[87] A. F. Garito, *Physics Today*, 1975, **28**, 17.

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MIXED VALENCE TYPE

$(OC)_5Re — GeMe_2—GeMe_2—Fe(CO)_4—GeMe_2—GeMe_2—Re(CO)_5$
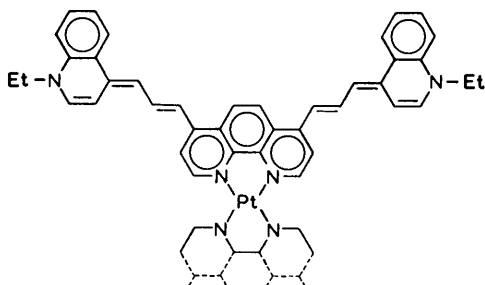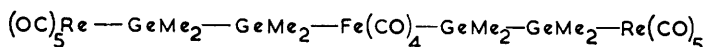
TRUE COVALENT TYPE

Figure 24 *Metal–metal bonded systems*

conductors[90] and it is possible that some are superconductors. Deoxyribonucleic acid (DNA) has a structure resembling Little's superconductor model but although the poly(sugar phosphate) backbone is periodic, the pendant pyrimidine and purine bases are placed aperiodically. Nevertheless Ladik[91] considers from a study of a periodic DNA model that the delocalized π-electrons from the bases might pair if they interact with the σ-electrons functioning as the polarizable side-chain electrons of Little's model. Moreover, in the case of the DNA double helix he thinks that the polarization of the π- and σ-electrons in one chain might give an attractive interaction between the π-electrons of the other chain and result in electron pairing.[91,92] Thus Ladik believes that it is possible for enhanced conductivity to occur in some regions of DNA at room temperature although this will not amount to normal superconductivity.

There is support for the view that certain parts of nerve fibre which have a high concentration of cholesterol are superconductive at physiological temperatures.[93] Halpern[94] found that the diamagnetism of the sodium salts of cholic, desoxycholic, lithocholic, and cholanic acids changed abruptly at 30, 60, 130, and 277 K, respectively, and these are thought to be superconductive transitions in small domains dispersed in the bulk insulating matrix. Goldfein[95] has now

[90] D. D. Ely, in 'Organic Semiconducting Polymers', ed. J. E. Katon, Edward Arnold, London, 1968, p. 259; E. O. Forster and A. P. Minton, in 'Physical Methods in Macromolecular Chemistry', ed. B. Carroll, Dekker, New York, Vol. 2, 1972.
[91] J. Ladik, G. Biczo, and J. Rédly, *Phys. Rev.*, 1969, **188**, 710.
[92] J. Ladik and A. Bierman, *Phys. Letters*, 1969, 29A, 636.
[93] F. W. Cope, *Physiol. Chem. and Phys.*, 1971, 3, 403; 1974, 6, 405.
[94] E. H. Halpern, 'High Temperature Non-metallic Superconductors', Naval Shipyard R. and D. centre, Annapolis, Maryland, 1973, report 3917.
[95] S. Goldfein, *Physiol. Chem. and Phys.*, 1974, 6, 261.

shown that the transitions are electronic in nature because there is no change in the atomic lattice structure. He also finds that the four bile acid salts obey the empirical rule of Matthias[86] which applies to superconducting transition-metal alloys, *i.e.* that T_c is proportional to the average number of valence (outer shell) electrons per atom. This indicates that high-temperature superconducting regions are present in these compounds.

Proteins are well known to show semiconductivity, which increases dramatically with the degree of hydration, but the mechanism of conduction is not known. Evidence is now appearing to suggest that proteins also may show superconductivity. Fröhlich[96] has found that a magnetic field of 600 G increases the diamagnetic susceptibility of a 0.01% aqueous solution of lysozyme by a factor of 10^4 times that expected for ordinary diamagnetic material. An increase in field to 800 G destroys the effect by what appears to be a room-temperature Meissner effect. Fröhlich thinks that small superconductive regions attached to each enzyme molecule are formed by some process involving water. These regions cluster together and lead to the enormous increase in diamagnetism.

These observations hold out the promise that room-temperature superconductivity will be realized. In biopolymers it is probably restricted to localized domains and so far no high or superconductivity has been observed as a bulk property. But biopolymers may hold the clue to the specification for a true superconducting polymer.

Thus so far no organic superconductor has been discovered. The emphasis is on achieving perfect long-range order for superconduction but how this could be embodied in a useful polymeric structure is not clear. However, ordered polymer structures exist and even if they are not perfect enough for superconduction it is certainly possible that they could provide sufficient organization to give metallic conductivity.

10 Conclusions

We have seen that polymers with high conductivity can be made. The main problem is to combine this with good processability and this is where stacked-planar systems are superior to conjugated polymers. But even then good mechanical properties have yet to be achieved. In some way the rigid π-bonded systems must be combined with a conventional σ-bonded polymer without destroying its flexibility and tensile properties. The structure will contain a radical-ion system to provide charge carriers but we do not know how to design the polymer structure to give high carrier mobility.

Conductive polymers might be expensive to make but this is less important in special applications. There is no doubt that a room-temperature superconducting polymer would be worth its weight in gold if it provided us with loss-free power transmission and friction-free magnetic bearings.

The work on organic superconduction has not failed. It has succeeded in showing that the first step forward must be to understand the organic metallic

⁹⁶ N. A. G. Ahmed, J. H. Calderwood, H. Fröhlich, and C. W. Smith, *Phys. Letters*, 1975. 53A, 129.

state. The second step comes as a challenge to polymer physicists to unravel the relationship between charge-carrier mobility and the supermolecular structure of polymers. This is most important as without it we cannot progress. Then as the third step chemists will have the opportunity to make a polymer with metallic conductivity and good mechanical properties. That achieved an organic superconductor is more likely to follow. But science must come before technology.