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# COMPOUNDS WITH CONJUGATED DOUBLE BONDS

V. V. Pen'kovskii

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## I. INTRODUCTION

The term "compound with conjugated double bonds" applies to a wide variety of organic substances, both monomeric and polymeric, and showing large differences in physical and chemical properties. We shall use it to describe a compound containing a fairly large number of carbon–carbon double bonds alternating with single bonds. The double bonds may include hetero-atoms, *i.e.* atoms with free electron pairs (such as N, O, S), without perturbing the conjugated system. These substances are intensely coloured, have a relatively high electrical conductivity, and show anomalous magnetic properties (electron paramagnetic resonance signals and static paramagnetism). We may arbitrarily classify these compounds into two general groups: 1) polymers with conjugated bonds and hetero--atoms in the conjugated chain, and 2) organic dyes. The second group includes polynuclear aromatic hydrocarbons, although these do not give an electron paramagnetic resonance signal.

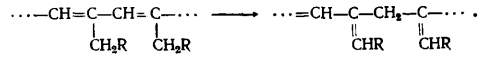
The special magnetic and electrical properties of polymers and other compounds with conjugated double bonds have received attention from many investigators in recent years[1–5]. In this review an attempt is made to expand systematically the results of the various investigators in this field, but monomeric or polymeric chelate compounds[6], polymers with a chain of metal atoms, or recently synthesised (and of independent interest) polymers with conjugated triple bonds[7] will not be considered here.

## II. METHODS OF PREPARATION

The preparation of dyes has been reviewed recently[8,9]. Polymers with conjugated double bonds are prepared by a variety of methods, the most important of which are listed below.

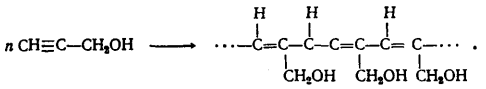
Polymerisation of acetylene hydrocarbons. Acetylene can be polymerised to give a system of conjugated bonds by various catalysts: aluminium ethoxide containing $TiCl_4$, titanyl or vanadyl acetylacetonates[10–12], sodium tetrahydroborate with a nickel halide[13] or an organophosphorus complex[14]. Polymerisation occurs between +80° and -80°; the number of units in the black, insoluble polymers is 12–15. Benzene is also formed in good yield.

The aliphatic homologues of acetylene undergo an analogous polymerisation[15], but they do not give conjugated systems, probably because of the isomeric rearrangement.



This type of rearrangement has also been reported in poly(cyclohexylacetylene) prepared by thermal polymerisation[16].

The polymerisation of acetylene can be induced by radiation at very low temperatures, giving a brown *cis*-polymer in the liquid phase and a dark red, insoluble *trans*--polymer in the solid phase[17]. Radiation polymerisation of propynol in the liquid or solid phase produces a dark red *trans*-polymer:



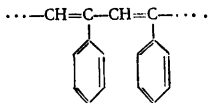
Phenylacetylene can be polymerised either by heating in an argon atmosphere or in the presence of air[18,19] for 6–12 h, or in the presence of a catalyst[19,20] at 80°. Initiators have little effect on the yield of the polymer, which does not exceed 30%. According to the polymerisation temperature used (150–400°), the resulting polymers vary in colour from yellow to black, the molecular weight also increasing with the depth of colour. The yield of polymer increases very significantly at polymerisation pressures of 98 and 588 MN $m^{-2}$†, reaching 66–67% at temperatures as low as 120°. The mean molecular weight of the polymer[21] can reach 1200. Alternatively, the yield of polymer can be increased by raising the polymerisation time to 18 h or by heating in solution in xylene or chlorobenzene

† 98 066.5 N $m^{-2}$ = 1 kgf $cm^{-2}$, in accordance with the SI international system of units [for the SI system see Russ.J.Inorg. Chem., 8, 1481, 1484 (1963) (Ed. of Translation)].

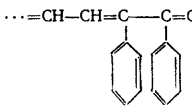
for 48–65 h. The yield of polymer is 75% in the first case, and practically quantitative in the second, but the mean molecular weight[22] does not exceed 1020.

The polymerisation of phenylacetylene can also be induced by irradiation with fast electrons or $\gamma$-rays[23,24], giving a molecular weight of up to 1700. The rate of polymerisation is independent of the dose rate, increases linearly with the integral dose of irradiation between wide limits, and is relatively insensitive to temperature.

It is assumed in all the above papers that the poly(phenylacetylene) molecules take up the "head-to-tail" (*i.e. trans-*) configuration with respect to the double bonds:



However, the "head-to-head" structure is proposed for poly(phenylacetylene) in a recent study[25] of the kinetics of its thermal polymerisation, in which various polymeric fractions of molecular weight 306–1700 were isolated.

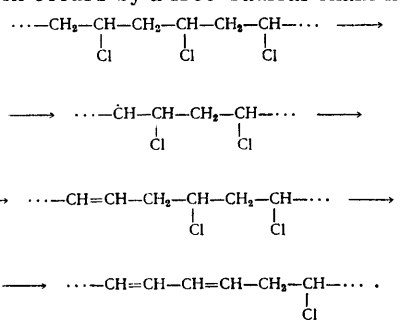


Polymerisation of the "head-to-tail" type is said to produce triphenylbenzene, and cause chain breaking.

It has recently been shown[26] that polymerisation of phenylacetylene on a Ziegler catalyst can give a product of mean molecular weight 5000, and polymerisation on copper oxide in a flow system (250–350°) can achieve a molecular weight of 7000. A mixture of aluminium ethoxide and bis-(dimethylglyoximato)iron gives an even higher degree of polymerisation when used as a polymerisation catalyst for phenylacetylene[27]: the mean molecular weight of the soluble fractions reaches 8900, and some insoluble products are formed as well. The total yield of poly(phenylacetylene) is almost quantitative.

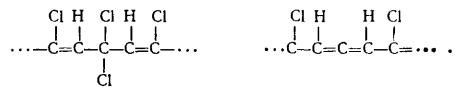
*p*-Diethynylbenzene polymerises easily on being heated, giving a three-dimensional polymer with conjugated bonds[28]. Furthermore, it gives copolymers with poly(phenylacetylene) and other substances. These processes are discussed in Section VII, Reactivity.

Intramolecular degradation of polymers. The most typical example of this is the formation of a conjugated chain in poly(vinyl chloride). The discoloration of poly(vinyl chloride) under the influence of light or of ionising radiation has long been recognised. However, Winkler[29] was the first to establish that a system of conjugated bonds, sometimes of quite appreciable length, is formed under these conditions as a result of loss of HCl. The degradation occurs by a free-radical chain mechanism:



The poly(vinyl chloride) molecule is branched, and at low temperatures (100–150°) the chlorine is not removed from tertiary carbon atoms: only the least stable parts of the macromolecule react under these conditions (allyl chloride and oxygen-containing groups[30]). At 190–200° the degradation occurs throughout the molecule.

Poly(vinylidene chloride) also becomes degraded with evolution of HCl, but in this case the conjugation can be perturbed (I), or allyl groups can be formed (II):



(I) (II)

The photochemical degradation of poly(vinyl chloride) also proceeds by a radical mechanism, initiated by light of wavelength[31,32] less than 310 nm. Irradiation of poly(vinyl chloride) with fast electrons or $\gamma$-rays produces chromophoric groups and polyene chains, giving rise to a colour varying from yellowish green to dark red, which gradually disappears at room temperature[33–36].

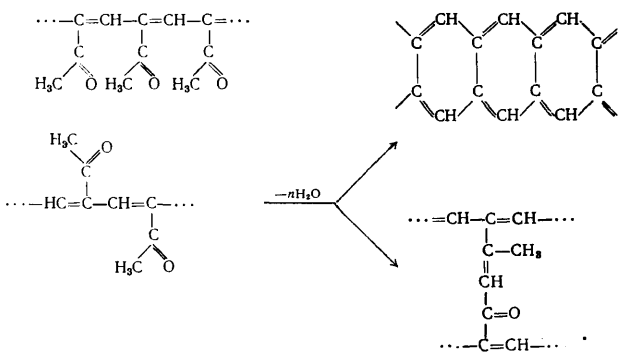
Poly(vinyl chloride) can be made to split off HCl also by chemical means. When poly(vinyl chloride) is treated with pyridine and a solution of alkali in methanol, a nitrogen-containing compound with conjugated bonds and a structure similar to that of cyanine dyes is formed[37]. A deeper (but still not complete) degradation is produced by the action of morpholine in a nitrogen stream[38] at 166°. The most effective dehydrochlorinating agents are the alkoxides, their efficiency increasing with the length of the alkyl chain (up to 99,6% dehydrochlorination has been reported[39]). The whole of the HCl is easily removed from poly(vinyl chloride) and poly(vinylidene chloride) with sodium pentyl oxide[40]. Treatment of poly(vinyl chloride) with potassium amide in liquid ammonia at room temperature gives a polyene containing 12% O, of composition[41] $CH_{1,12}O_{0.11}$. The dehydrochlorination of poly(vinyl chloride) by alkali treatment requires the presence of zinc chloride and a temperature[42] of 250°.

A linear or three-dimensional polyene is easily formed by heating poly(vinyl bromide). This material can be shaped and heat-treated to give filamentary or massive specimens of polyene[43].

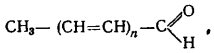
Poly(vinyl acetate) can also give a polyene with evolution of acetic acid, but this type of thermal degradation occurs only at 300° *in vacuo*[44]. A conjugated structure can be obtained much more easily by treating poly(vinyl acetate) with *p*-toluenesulphonic acid in benzene or toluene solution; as in the case of poly(vinyl chloride), loss of acetic acid occurs also at positions removed from the double bond, but the conjugated sections are of different length and are frequently interrupted[45].

After prolonged (20–30 d) standing, followed by treatment with glacial acetic acid to remove the HCl, 2-chlorovinyl methyl ketone forms a black, insoluble polymer[46] of suggested structure $H-[C(COCH_3)=CH]_n-Cl$. In the presence of iron(III) chloride the removal of HCl is much faster. The reaction is best carried out in sealed ampoules, because appreciable quantities of the trimer are formed in an open vessel or in solution. Heating the polymer to 300–700° under 1600 N $m^{-2}$ pressure increases the carbon content in the polymer; it is thought[47] that further polymeric condensation of the product occurs under these

conditions, both intramolecularly, to give six-membered rings, and intermolecularly:



The formation of an insoluble, coloured polymer has been observed during the polymerisation of vinyl acetate in the presence of boron trifluoride[48] or alumina–silica gel with an acidic surface[49]. In both papers, the polymer is assumed to contain a system of conjugated double bonds. It seems likely that hydrolysis of the vinyl acetate occurs first, followed by polymerisation and dehydration to give a polyene chain. The possibility of the second stage was demonstrated[50] by preparing a dark substance showing all the properties of a conjugated system, of probable structure

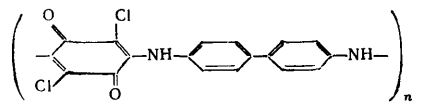


from acetaldehyde adsorbed on silica gel. The formation of polyene chains from vinyl acetate and acetaldehyde in the presence of silica gel occurs at room temperature.

When polyethylene is irradiated with neutrons or fast electrons, *trans*-vinylene bonds are formed, but not in large numbers: one double bond per 200 carbon atoms[51] after 4.65 MJ kg$^{-1}$. At the same time, cross-linking of the polyethylene molecules occurs. Irradiation in the air produces even fewer double bonds and less cross-linking in the polymer.

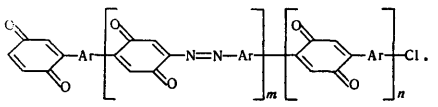
Polyethylene has also been irradiated in a reactor (11.2–250 MJ kg$^{-1}$) with subsequent heating in air[52] to 250–900°. The irradiation appears to give rise to six-membered saturated rings; the formation of conjugated double bonds is brought about by the subsequent oxidation of the polymer. The products of irradiation and heat treatment are black, infusible powders.

Polymeric condensation of diamines with carbonyl compounds. The reaction of chloranil with benzidine in alcohol, in the presence of sodium acetate, produces black infusible materials[53,54] to which the following structure has been ascribed:

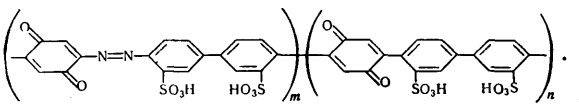


In a medium of dimethylformamide the chlorine atoms can be replaced by acetate groups. Similar polymers have been prepared by the reaction between *p*-benzoquinone and *p*-phenylenediamine, or benzidine and 3,3-benzidinedicarboxylic acid[55]. The terminal groups are amino-groups with chloranil and quinone groups with benzoquinone, the number of monomer units is 5–10.

Polymeric compounds are obtained also if the appropriate bisdiazo-compounds are used instead of the diamines[56]. The structure of these polymers is the following (where Ar denotes an aromatic residue):

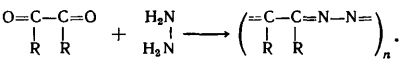


The number of polymeric links is 5–15. Azo-groups are retained in the polymer because of incomplete decomposition of the diazo-compounds. They cannot be completely removed, but polymers containing as little as 0.5% of nitrogen have been prepared. Polymers have been prepared, by the same method, from the diazo-compound of 4,4′-diaminobiphenyl-3,3′-disulphonic acid, taken in threefold and fourfold excess over benzoquinone[57]:



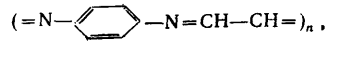
The nitrogen content of this polymer is 0.55–0.75%.

Polymeric condensation can occur also through carbonyl groups. Thus, the reaction between hydrazine and diacetyl or other diketones, and also with glyoxal, yield polyazines[58,59]:



The carbonyl groups can be separated by intervening atoms or groups. Polyazines containing oxygen and sulphur atoms in the chain, and also $CH_2$, $OCH_2$, and $C_6H_4$ groups, have been synthesised in this way. The glyoxal derivative is black, the other polymers vary from light green to orange in colour. The number of units in the polymer is 23–25 with benzil, and probably higher still with glyoxal, but it falls to 4–7 when intermediate groups are introduced into the chain.

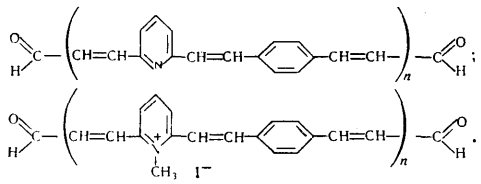
The polymeric condensation of glyoxal, terephthalic aldehyde, and diacetyl with *p*-phenylenediamine at 80° leads to the formation of polymeric Schiff bases[60]. In the last two cases the chemical composition of the polymer agrees with that calculated for a dimeric product. The number of monomer units in the polymer



has not been determined.

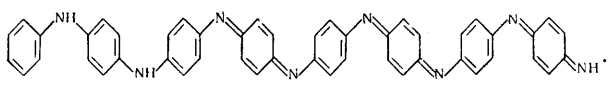
Aromatic dialdehydes, when condensed with 2,6-lutidine at 160–220° or with *N*-methyllutidinium iodide at 70–90°.

give brown infusible polymers which probably have a linear structure[61]:



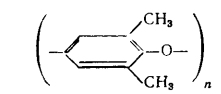
The number of polymeric units is 9–11 in the former material, 4–7 in the latter.

Oxidation of aromatic amines and phenols. The product of the oxidation of aniline by potassium dichromate (aniline black) has been known for a long time, but its structure is not fully characterised despite the large number of investigations devoted to it[62–64]. We only know with certainty that aniline black belongs to the class of polymers with conjugated double bonds. The product of the oxidation of aniline by potassium chlorate, nigraniline, also belongs to this class[62,64], as is clear from its formula:



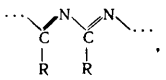
The oxidation of aniline, diphenylamine, and triphenylamine by sulphuric acid leads to the formation of dark-coloured products reminiscent of aniline black, but containing sulphur[65].

Linear polyphenylene oxides may be formed during the oxidation of sterically hindered phenols, owing to the stability of the phenoxy-radicals. Thus, when air is passed through a solution of 2,6-dimethylphenol in pyridine in the presence of copper(I) chloride, a linear polymer of the following structure is formed[66,67]:



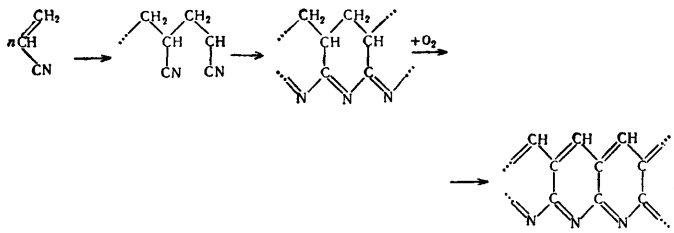
Oxidation proceeds with the participation of $Cu^+$ ions, since the same polymer can be obtained also in the absence of oxygen. Products of similar structure are formed from 4-chloro- and 4-bromo-2,6-dimethylphenol[68], and also from 2,6-diethylphenol, 2,6-diphenylphenol, and other compounds of this class[69].

Polymerisation of compounds containing the CN group. When hydrocyanic acid is refluxed with aqueous ammonia or potassium cyanate, a dark brown, insoluble polymer is formed. This compound, an acylaminic acid, has a cyclic structure and contains amino-groups[70]. Aliphatic and aromatic nitriles can form, in the presence of metal chlorides, linear polyconjugated systems of the type



whose properties depend on the polymerisation time[71].

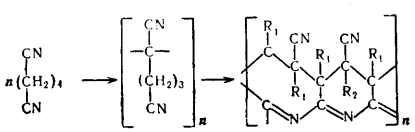
Polymerisation of acrylonitrile, followed by heat treatment at 400–500°, yields coloured polymers[42,72,73]. The relevant processes here are the formation of condensed six-membered rings and their dehydrogenation:



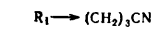
Previous irradiation at -196° lowers the temperature at which conjugated chains appear in polyacrylonitrile to 135–175°.[17]

Heat-treatment of poly(methacrylonitrile) also produces the conjugated chain –C=N–C=N–, but aromatisation of the rings does not take place because there are no CH groups[74]. The formation of conjugated bonds is accelerated by nucleophilic reagents such as acids, which can form copolymers with the substance or remain within the polymer. Cyclisation of poly(methacrylonitrile) can also be induced by irradiation in the liquid or solid phase[17].

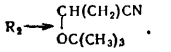
The formation of cyclic structures is not confined to hydrogen cyanide and poly(acrylonitrile). Polymerisation of tetracyanoethylene at 200° in the presence of catalysts[75] also leads to a black product for which a structure similar to that of porphyrin has been proposed. Cyclic polymers can be obtained also from aliphate nitriles, but this requires either irradiation in the solid phase[17] or a stronger oxidising agent than atmospheric oxygen. Treatment of glutaronitrile or of the nitrile of methylmalonic acid with an excess of t-butyl peroxide produces black powdery polymers having a cyclic structure[76], which are formed by the scheme:



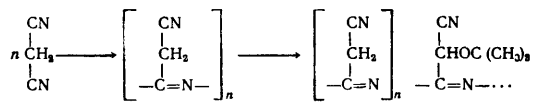
where



and



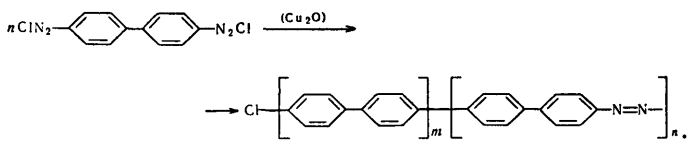
A polymer of malononitrile is formed at a 2.5 : 1 molar ratio of nitrile to peroxide, but it is not cyclic:



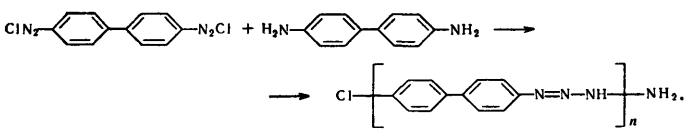
The number of monomer units in the polymer can be as high as 90–100. This process is a typical application of the polymeric recombination reaction[77].

Polymerisation of bisdiazonium compounds. This rather specialised method of preparation of

polymers with conjugated double bonds consists in the low-temperature polymerisation of the bisdiazonium compounds of aromatic diamines in the presence of copper(I) oxide[78,79]:

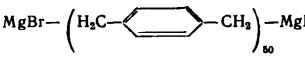


The products of this reaction are known as polyazophenylenes. Complete removal of the azo-groups from the polymers has proved impossible so far. Nonetheless, the conjugation of the polymers is not disturbed, due partly to the linearity of their structure. Later, polyazophenylenes with various substituents in the benzene rings ($CH_3$, COOH, etc.) were also prepared[80-82]. The bisdiazonium salt of benzidine copolymerises with benzidine, giving a linear polytriazine[83]:



Starting from the bisdiazonium compounds of 4,4′-diaminodiphenylmethane and 4,4′-diaminodibenzil, polymers with $-CH_2-$ and $-CH_2CH_2-$ groups between the benzene rings have been prepared[84]‡.

Wurtz reaction. Using this simple method, polyphenylenes[85,86] have been obtained from *p*-dichlorobenzene, and polyxylylenes and polyphenylenemethylenes[87,88] from compounds of the type $ClCH_2-Ar-CH_2Cl$ (where Ar is an aromatic hydrocarbon residue). The polymers were strongly branched in both cases. The action of magnesium on *p*-xylylene bromide gave a polymer[89] of composition

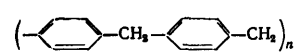


Polymerisation of aromatic compounds in the presence of metal chlorides. Benzene (1 mole) rapidly polymerises to poly-*p*-phenylene[90] in the presence of aluminium chloride (0.5 mole), copper(II) chloride (0.5 mole), and water (1 ml), at 36–37°. The reaction does not proceed in the absence of either of the chlorides. Replacement of the copper(II) chloride by iron(III) chloride seems to lead to polymers with a cellular structure, since their C : H ratio fluctuates between 1.8 and 2.5.

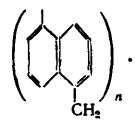
The same method can be used to prepare polymers with methylene groups in the chain, *e.g.* from dichlorethane and halogen-substituted benzenes, and also from biphenyl, benzene, and dibenzyl[91,92]. The catalyst is aluminium chloride.

‡ Strictly speaking, these polymers do not possess a system of conjugated bonds, and their assignment to the type being discussed here is justified only on the basis of their magnetic properties. The correctness of this point of view is examined in Section VIII, Theory. For comparison, other methods of preparation of polyphenylenes (containing $-CH_2-$ groups) are described below.

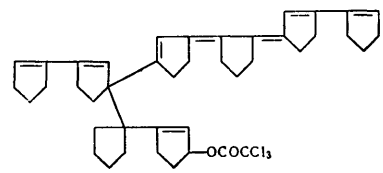
The polymeric condensation of benzyl chloride and α-chloromethylnaphthalene has been accomplished[92] in the presence of chlorides of Group IV elements: the effect of titanium chloride was examined both with the pure monomer and in solution. Silicon and thorium chlorides are the least active. This reaction gave polymers of the type



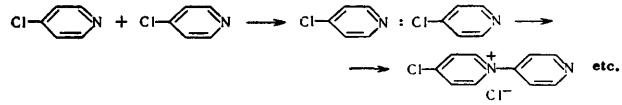
and



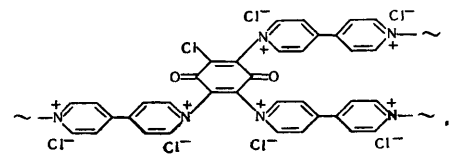
Other methods. Cyclopentadiene slowly polymerises in the presence of trichloroacetic acid, forming a system of conjugated double bonds:[94]



The polymerisation proceeds by an anionic mechanism; the number of units is not large. A polymer with conjugated bonds can also be obtained[95] by the onium polymerisation of 4-chloropyridine at 50–60°. The mechanism of this process is described by the scheme

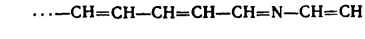


The reaction products are yellow and contain 8–14 pyridine nuclei. A copolymer of 4,4′-bipyridyl with chloroanil, having the structure



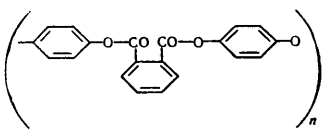
has also been prepared.

Heating the complex of pyridine with zinc chloride $ZnCl_2(C_5H_5N)_2$ to 375–400° in a dry inert medium causes fissure of the pyridine ring with formation of the linear polymer[96]:

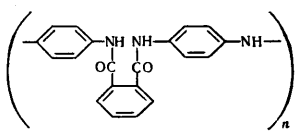


In the presence of 0.5–6.0% of $HPO_3$ the reaction occurs even at 330°. The yield and molecular weight of the polymer increase to some limiting value, depending on the temperature of the experiment, at high concentrations of $HPO_3$.

Zinc chloride promotes various polymeric condensation processes, such as the reaction between phthalic anhydride and hydroquinone or *p*-phenylenediamine at 250°, giving polymers with heteroatoms in the conjugation chain[42]:



and



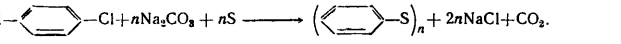
Polymeric condensation with phenols to give conjugated systems has been reported also in the case of anhydrides of other polybasic acids[97].

Aldehydes and ketones containing a methyl group are also capable of undergoing polymeric condensation in the presence of a large excess of zinc chloride or other chlorides[98]. The resulting polymers again contain conjugated bonds of the type $(CR{=}CH)_n$. The polymeric condensation of acetaldehyde proceeds at 70°, that of ketones at 180–200°.

Polyphenylenes can be prepared by prolonged (several hours) heating of organolithium compounds LiArLi, where Ar = *p*-phenylene or 4,4′-diphenylene, in ether in the presence of cobalt bromide[99]. The reaction is

$$n\,\mathrm{LiArLi} + (n-1)\,\mathrm{CoBr_2} \longrightarrow \mathrm{Li(Ar)_nLi} + (n-1)\,\mathrm{Co} + 2(n-1)\,\mathrm{LiBr}.$$

Polyphenylene sulphides[100] can be obtained by fusing *p*-dichlorobenzene with sodium carbonate and sulphur:



These polymers show strong branching. Linear polyphenylene sulphides result from the autocondensation of the sodium salt of 4-chlorothiophenol[101].

## III. SOLUBILITY

Most polymers with conjugated double bonds are sparingly soluble, the solubility decreasing as the depth of colour increases. The black polymers are insoluble, as a rule. Only when nitrogen atoms are present in the conjugated chains can such polymers dissolve in concentrated acids and in some polar solvents: this has been demonstrated for poly(aminoquinone)s[56], aniline black[63], poly(azophenylene)s[80], and polytriazenes[83]. Polymeric nitriles are insoluble, however. A high proportion of the poly(phenyl sulphide) polymer is soluble in diphenyl ether[101], but up to 20% of the material does not dissolve.

Poly(phenylacetylene) and polycyclopentadiene are fairly readily soluble in benzene and other organic solvents, possibly because of the small number of monomer units in the polymeric chains[18-20,94]. The low-molecular-weight fractions of poly(azophenylene)s and polytriazenes ($M$ = 600–700) are also soluble in benzene and acetone, and can be extracted from the main bulk of the polymer[80,83]. The specific viscosity of solutions of high-molecular fractions of these polymers goes through a maximum when plotted against concentration: this confirms that macromolecules of the polymers have a linear structure and show association. Substituents in the benzene rings of the polymers weaken the association of the macromolecules in solution.

## IV. MAGNETIC PROPERTIES

Polymers with conjugated double bonds. The most characteristic feature of these polymers, which distinguishes them from other high-molecular-weight compounds, is the presence of a single, narrow electron-paramagnetic resonance (EPR) signal with a $g$-factor of 2.003, *i.e.* corresponding to a free electron. There have been no reports of any hyperfine structure in the EPR spectra of these polymers. The concentration of unpaired electrons per gramme of the material differs very considerably in the different polymers: from $2.4 \times 10^{17}$ for phenylacetylene[18] to $8.7 \times 10^{19}$ for some poly(azophenylene)s[81]. The width of the line between the points of maximum slope is 0.6–1.4 mT§ [millitesla (Ed. of Translation)]; a narrower signal is found in heat-treated poly(azophenylene)s[81] (0.3–0.6 mT), and in irradiated polyethylene[52] heated to 500–700° and evacuated to 266.6 $\mu$N m$^{-2}$¶ (50 $\mu$T). In both cases the narrowness of the signal is associated with the thermal treatment of the polymer. When the polymer is dissolved, neither the shape nor the magnitude of the signal are changed[19,102]†.

Poly(azophenylene)s which have not been heat-treated give a second signal of width 2.6–3.5 mT, superimposed on the first, and also a triplet signal with a $g$-factor of 2.05; both these signals disappear when the material is heated[81] to 300°. A fairly broad EPR signal 2.5–2.5 mT is obtained with heat-treated polyacrylonitrile[42,73] and irradiated poly(vinyl chloride)[33]. The half-width of the line for the latter material has been given[103,104] as 5.3 mT. The EPR spectrum of the oxidation products of aromatic amines by sulphuric acid contains a line of width[65] ~5.0 mT; for aniline black the width is[105] 1.1–1.3 mT, and for its hydrochloride[106] 0.6 mT.

In chemically dehydrochlorinated poly(vinyl chloride) the line width is[39,44] 1.1–1.2 mT. In polycyclopentadiene the signal depends on the length of the polymer chain, since it appears only 20 h after the beginning of the reaction[107]; as the number of monomer units in the polymer changes from 5 to 11, the concentration of unpaired electrons increases by one order of magnitude[108].

The EPR spectra of polyvinylenes, prepared from poly(vinyl chloride), are significantly altered by oxygen: in air the EPR spectrum is either converted into an asymmetric signal typical of peroxidic compounds[33] or disappears[41]. Organic peroxides have a similar effect[40]. Heating the material to 400° in a vacuum or in air restores the original signal. Conversely, polycyclopentadiene gives a stronger signal in air than at 1.333 N m$^{-2}$, but further

§ 1 T = $10^4$ G, in accordance with the SI international system of units.

¶ 133.322 N m$^{-2}$ = 1 mmHg, in accordance with the SI international system of units.

† Solutions of poly(phenylacetylene) show a poorly resolved hyperfine structure[185].

evacuation to 13.33 $\mu$N m$^{-2}$ does not alter the signal[107]. The width of the polyethylene line decreases[52] after vacuum heat-treatment. For the remaining polymers, the intensity and width of the signal remain the same in the air and in an inert medium (nitrogen, argon).

When polymers with conjugated bonds are heated, whether in a vacuum or in air, the concentration of unpaired electrons does not normally alter. The only exception are polymers containing only carbon and hydrogen. Heating poly(phenylacetylene) (prepared at 150°) to 300° or 400° raises the concentration of unpaired electrons by one or two powers of ten respectively[19]. The EPR signal of polycyclopentadiene decreases with increasing temperature from -198° to 60°, becomes stronger at higher temperatures, and begins to drop again above 120°. The latter effect is more significant the higher the molecular weight of the polymer fraction[108]. Conversely, the concentration of unpaired electrons decreases when poly(diethynylbenzene) is heated, and at 500° *in vacuo* the signal disappears[28]. The intensity of the signal from dehydrated polyacetaldehyde decreases on heating to 200°; the effect is completely reversible[50].

In addition to narrow lines, the EPR spectrum of aniline black[105,106] and poly(aminoquinone)s[102,109] contain some broad lines (over 10 mT wide). The wide EPR signal reported for bisdiazonium copolymers with quinones[3] was not confirmed by later work[84]. These lines are similar to those found in the EPR spectra of antiferromagnetics (MnO, $Cr_2O_3$). The $g$-factor of the centre of the broad lines is different from the free electron $g$-factor; the calculated apparent concentration of unpaired electrons per gramme of the polymer[109] can be as high as $10^{21}$.

Introduction of methylene groups into poly(azophenylene)s causes a sharp decrease in the number of unpaired electrons, but if the benzene rings are separated by two methylene groups the signal persists[84]. Poly(arylmethylene)s prepared by other methods have not been examined by EPR.

The magnetic susceptibilities of poly(phenylmethylene)s and poly(naphthylmethylene)s prepared in the presence of Group IV metal chlorides have been measured[93]. Poly(phenylmethylene)s are diamagnetic irrespective of the type of catalyst ($\chi = -0.571 \times 10^{-6}$ cm$^3$ g$^{-1}$). Poly(naphthylmethylene) prepared by block polymerisation in the presence of $TiCl_4$ is also diamagnetic ($\chi = -0.045 \times 10^{-6}$ cm$^3$ g$^{-1}$). The other polymers of this class are paramagnetic; their magnetic susceptibility depends on the type of catalyst, and reaches the value $+1.441 \times 10^{-6}$ cm$^3$ g$^{-1}$ after polymerisation in the presence of $SiCl_4$.

Compacted poly(diethynylbenzene), heated at 170° in a nitrogen stream, is weakly paramagnetic; beyond 400° its susceptibility becomes negative, and beyond 500° it becomes positive once again[28]. Concentrations of unpaired electrons calculated from magnetic susceptibilities do not agree with those derived from EPR spectra.

The magnetic susceptibility of poly(phenylacetylene)[102] increases with molecular weight from $0.20 \times 10^{-6}$ to $2.6 \times \times 10^{-6}$ cm$^3$ g$^{-1}$‡; poly(phenylacetylene) of low molecular weight is diamagnetic, $\chi = -0.6 \times 10^{-6}$ cm$^3$ g$^{-1}$. Blyumenfel'd *et al.* conclude[102] that the EPR signal reflects the properties of the individual macromolecule, whereas the magnetic susceptibility of the polymer is determined by its structure. The increase in magnetic susceptibility of poly(aminoquinone) after heating and addition of copper, and in that of poly(tetracyanethylene) after heating, are quoted in support of this hypothesis.

Poly(phenylacetylene) and poly(aminoquinone) show a characteristic saturation of the magnetic susceptibility with increasing field strength, similar to that of ferromagnetic materials[102]. The magnetic susceptibility of polytriazine, equal to $+0.55 \times 10^{-6}$ cm$^3$ g$^{-1}$, is independent of the field strength[83].

The nature of the anomaly in magnetic properties found in polymers with conjugated double bonds has been discussed repeatedly. Great interest was aroused by the first reports of broad EPR lines, and "ordered regions" were assumed to be present in polymers with conjugated bonds by analogy with ferromagnetic domains in which electrons can move freely[102]; the extent of these regions was thought to depend on structural factors. It was even suggested that wide lines should be regarded as a general property of polymers with conjugated bonds. The obvious absence of broad lines in the spectrum of poly(phenylacetylene) was interpreted as being due to an extremely wide line, or to measurements below the Néel point. However, the "ferromagnetic" and "antiferromagnetic" properties of polymers could be due to small amounts of paramagnetic impurities[110], to which the EPR method is very sensitive. False paramagnetism, which disappears upon the removal of impurities, has been demonstrated in other materials by EPR.[111] The broad line in the EPR spectrum of aniline black[106] is caused by the presence of $Cr^{3+}$ ions, and disappears when these ions are removed.

The saturation level of magnetisation of various polyvinylidenes has been measured[112]. The amounts of iron oxides needed to explain the results were compared with those found experimentally. In the case of poly(phenylacetylene) the effect is undoubtedly caused by 0.01% of iron impurity; for other polymers the calculated amount of iron is higher than the experimental but in poly(diethynylbenzene) they are of the same order of magnitude. No broad EPR lines were observed. It was suggested that the regions of ferromagnetic inclusions are closely bound up with the organic structure of the polymer.

The view that wide lines are a characteristic of all polymers with conjugated bonds has again been upheld: in polyvinylenes the line becomes saturated at microwave power because of the strong spin–orbital relaxation. Results on wide EPR lines in polymers with conjugated bonds, and their interpretation, are obviously in need of clarification.

The triplet signal in poly(azophenylene)s, with a $g$-factor of 2.05–2.06, could also be due to impurities, although it has been ascribed[81,84] to unreacted macro-radicals. The latter do, however, account for the line of width 2.5 mT and $g$-factor 2.00 which is observed in irradiated poly(vinyl chloride) and poly(acrylonitrile), and also in poly(azophenylene)s.

The reason for the appearance of the narrow singlet signal is discussed in Section VIII, Theory.

Dyes and other compounds. A narrow EPR signal with a $g$-factor of 2.003, very similar to the signal given by polymers with conjugated bonds, has been observed in Lacmoid[113], and in cyanine[114] and triphenylmethane[115] dyes. Its intensity increases when the materials

‡ Somewhat different, but apparently less accurate, results have also been reported[19].

are cooled to -196°, and also when the pressure is reduced to 1.333 N $m^{-2}$ and beyond. The effect of dissolution of the dye on the EPR spectrum was not established in the cases of cyanine dyes[114], but with triphenylmethane dyes it was shown that dissolution causes loss of the signal[115].

In solutions of Lacmoid the signal persists: it disappears only if the solid is heated to 730°.

Cyanine dyes give an EPR signal only if their polymethyne chain exceeds a certain length: for example, there is no signal in dyes bound by a single CH group. As the chain becomes longer, the width of the line decreases[114]. Unfortunately, the materials used in this work were not always pure, and this caused apparent exceptions to the above rule for pseudocyanines, and the alleged "discovery" of a broad signal ($g$ = 2.240) in one of the thiacyanines.

Phthalocyanines also give an EPR signal. According to some workers[116], the signal is given only by $\alpha$-phthalocyanine, obtained from the $\beta$ form by reprecipitation from concentrated sulphuric acid followed by careful washing. $\beta$-Phthalocyanine, extracted by nitrobenzene and sublimed in nitrogen, does not give a signal. These reports were not confirmed, however, by later work[117], in which a weak EPR signal was occasionally (but not invariably) detected in the $\alpha$ modification, and a strong signal in the $\beta$ modification, collected after repeated filtrations of phthalocyanine solutions in pyridine and dioxan. However, when the $\beta$-phthalocyanine was prepared by heating $\alpha$-phthalocyanine *in vacuo* at 300° no signal was observed.

A broad line ($g$ = 2.19, width ≃ 0.16 T) was noted[118] in the spectrum of metal-free phthalocyanine, and ascribed to collective interaction of unpaired electrons, although the possibility of paramagnetic impurities was admitted. The intensity of the signal increases on cooling the material, whilst dissolution in concentrated sulphuric acid suppresses the EPR signal of phthalocyanine completely.

Other workers[119] failed to detect broad lines in the EPR spectrum of "metal-free" phthalocyanine. Attempts at removing impurities by subliming the "metal-free" phthalocyanine in oxygen, nitrogen, or vacuum at 500° proved unsuccessful, since their signal persisted§. Therefore, the narrow EPR signal of phthalocyanine was ascribed[119] to the presence of impurities with an unfavourable separation factor, or to partial carbonisation.

This conclusion reappears in a number of other papers on EPR signals in dyes. Thus, no signal was found[120] in carefully purified $\beta$-carotene either in air, or in vacuum, or after heating to 130°, whereas $\beta$-carotene which has not been purified gives a strong signal[121]. The "impurity" approach to the EPR signal is most rationally developed by Kholmogorov and Glebovskii[122], who prepared a sample of phthalocyanine not giving an EPR signal by multiple reprecipitations from sulphuric acid; by contrast, the phthalocyanine precipitated from the filtrate and sublimed in a vacuum gave a signal 0.4–0.7 mT wide. Also, their original samples of triphenylmethane dyes[122] gave no signal, and only after heating them in air to 200° did a signal appear (owing to partial oxidation). The EPR signal of certain cyanine dyes is also due to oxidation products which can form even at room temperature. Thus, all the EPR spectra observed in dyes can be ascribed to the effect of impurities difficult to remove from the parent substance and which are apparently of high molecular weight, since they are formed by resinification: yet, no direct proof of the formation of such impurities during the oxidation of dyes has been given[122]. The broad EPR lines in phthalocyanines and nigrosine are unmistakably due to paramagnetic metal ion impurities.

We cannot, of course, ignore oxidation effects in dyes: this is shown by the influence of oxygen on the EPR spectrum of cyanine dyes[114], and by the appearance of an EPR signal upon oxidation of phenothiazine[123]. But there are no grounds for ascribing to them all reported EPR spectra in dyes, even though high-molecular oxidation products would go into solution with difficulty, and would always be expected to be present in the precipitate if they are present in the filtrate. To throw some light on this problem, the EPR spectra and the magnetic susceptibility of triphenylmethane dyes synthesised in a diamagnetic vessel and carefully purified have been investigated[124]. A narrow EPR signal was observed in every case, in complete agreement with previous work[115]; anisotopic diamagnetism was also detected, suggesting delocalisation of $\pi$ electrons in the molecule. When the dyes are dehydrated there is a sharp drop in diamagnetic susceptibility, which can only be explained by an increase in the paramagnetism of the material resulting from the removal of the dipolar water molecules. The signal disappears in solutions, and is restored when the dye is precipitated. Thus, the paramagnetism of triphenylmethane dyes, and probably also of other dyes, is an intrinsic property of the solid phase of these materials: it arises from the same causes as the magnetism of polymers with conjugated double bonds. These are discussed in Section VIII, Theory.

Phenazhydrine in the solid state also gives a narrow EPR signal with a $g$-factor typical of a free electron, and which disappears in solution[125]. The intensity of the signal increases by a factor of 2–3 after heating at 120° for 30 min, but does not increase any further at this temperature.

Light-induced EPR signals in dyes have been reported in various papers. Thus, when cyanine dyes adsorbed on silver bromide are illuminated, a narrow signal ($g$ = 2.005) is observed[126] at -196°. Heating to room temperature suppresses the signal, but on cooling and illumination the signal reappears. The cycle can be repeated several times. The intensity of the signal is higher in vacuum than in air. This behaviour has been ascribed[127] to oxidation of the dye by the bromine formed by photodecomposition of silver bromide: addition of bromine to dyed silver bromide in the dark does, in fact, induce a narrow EPR signal. The concentration of unpaired electrons on illumination is $10^{13}$–$10^{14}$ per 0.4 g silver bromide which has absorbed the dye from a $10^{-4}$ M solution.

Illumination of triphenylmethane dyes in a vacuum of 13.22 mN $m^{-2}$ at room temperature produces a narrow signal which decays in the dark[128]. Admission of oxygen and quinone vapour suppresses the signal in some cases (Malachite Green, Crystal Violet), and increases it in others (Bengal Pink, Phloxin). This effect is entirely analogous to the effect of electron acceptors on the conductivity of dyes if we identify the current carriers with electrons in the former case and with positive holes in the latter.

These observations provide further confirmation of the generality of the causes of anomalous magnetic and electrical properties in compounds with conjugated double bonds.

§ However, the phthalocyanine was transferred from the sublimation apparatus to its container in the air: this could have caused partial oxidation.

## V. ELECTRICAL PROPERTIES

Polymer with conjugated double bonds. As we stated above, polymers with conjugated double bonds have a fairly high electrical conductivity owing to the presence of a well-developed system of $\pi$ conjugation and electron delocalisation. It should be noted that the $\pi$ electrons in these polymers must have sufficient energy to permit tunnelling transitions through the intermolecular barrier if the electrical conductivity of the polymer is to have a significant magnitude [129]: thus, macromolecular orientation and structural effects play a significant role, as well as electron delocalisation, in determining the electrical properties of polymers.

The electrically conducting polymers first investigated were the products of the high-temperature pyrolysis of vinyl polymers [1,5,43,130-132]. The conductivity of the product increases with pyrolysis temperature: heating to 700° gives a value of $\sigma = 100$ $\mu$S m$^{-1}$¶, whereas $\sigma = 100$ S m$^{-1}$ is obtained at 800°. The pyrolysis products have an extensive three-dimensional structure of six-membered rings, and a low hydrogen content (1–3%). They can be regarded as intermediate between linear polymers with conjugated bonds and products of carbonisation (coals, graphite). The electrical conductivity of the pyrolysis products of all vinyl polymers varies exponentially with temperature: $\sigma = \sigma_0 \exp(-\Delta E/2kT)$.

This relationship characterises all polymers with conjugated bonds, but it is nevertheless possible to classify these polymers into two groups according to their electrical properties.

Polymers of the first group have a structure consisting of condensed rings. Their electrical conductivity is high (1 mS m$^{-1}$–10 nS m$^{-1}$), and their forbidden gap is not very wide (< 0.08 aJ)†, which makes them very similar to inorganic semiconductors. One such "organic semiconductor" is pile irradiated or heat-treated polyethylene [52,133], in the temperature interval from -25° to +150°. An increase in integral radiation dose, or especically in the temperature of heat treatment, lowers the activation energy $\Delta E$ and increases the conductivity.

High electrical conductivity is found also in oxidised polyvinylene, heated in a vacuum [40] to 150°, and in the degradation product of poly(vinyl chloride) heated in air [134] to 400°. Condensed aromatic structures are apparently formed in both cases. Yet, when poly(vinyl chloride) is heated to 500° in a nitrogen atmosphere (*i. e.* without oxidative dehydrogenation) its electrical properties are close to those of an insulator [124].

The first group includes also heat-treated polyacrylonitrile [42,73], whose electrical conductivity at 20° ranges from 20 $\mu$S m$^{-1}$ to 2 kS m$^{-1}$, with an activation energy of 0.037–0.125 aJ, depending on the temperature of heat-treatment [135]. The electrical conductivity of tetracyanethylene polymers is close to 0.1 $\mu$S m$^{-1}$ at room temperature, and there is only one report [75] of its reaching 10 $\mu$S m$^{-1}$. The activation energy and the pre-exponential term depend on the type of polymerisation catalyst used.

The effect of oxygen on the electrical conductivity of these polymers is not unique. With heat treated polyethylene, oxygen increases the electrical conductivity of the system. However, beyond a certain temperature (which depends on the heat-treatment temperature) this relationship no longer applies [52]. Heat-treated polyacrylonitrile has an electrical conductivity showing a distinct "oxygen effect" [136,137]: after heating to 420° in a high vacuum, the electrical conductivity of the specimens increases by one order of magnitude, but it recovers its original value in the air. The smallest effect is observed in specimens heated to the highest temperatures (670–730°). At the same time, the thermoelectric power of the polymers becomes negative‡, whereas before heating *in vacuo* it was either negligible or large and positive. This effect is also reversible. The thermoelectric power of conducting polyethylene, on the other hand, increases in an oxygen atmosphere and remains positive [52].

The properties of semiconducting polymers can be altered also by treatment with halogens. Adsorption of iodine at 20° raises the electrical conductivity of "conducting" polyethylene by five powers of ten [138]. The temperature variation of the electrical conductivity of the polymer remains exponential from -80° to +20°, with a value of $\Delta E$ unchanged by the iodination. Above 125° the increase in conductivity stops, and on cooling the specimen a different temperature law is observed: this is probably characteristic of the product of the reaction between the polymer and iodine. The Seebeck coefficient of iodinated polyethylene is positive, and increases with temperature.

Adsorption of iodine in a vacuum at 240° increases both the electrical conductivity of polyethylene and the value of $\Delta E$. At higher temperatures the conductivity type of the polymer changes. The manner in which the electrical properties of the polymer change with temperature corresponds to the transition from impurity conduction to intrinsic conduction observed in inorganic semiconductors. The value of $\Delta E$ calculated theoretically is in good agreement with the experimental value. It is assumed that iodine (and oxygen) can lower the potential barriers between the units taking part in multiple conjugation in the polymeric macromolecules, and thus raise the carrier mobility. This hypothesis is supported by the decrease in the "oxygen" and "iodine" effects in polymers having extensive structures following high-temperature treatment.

The thermoelectric properties of various polymeric nitriles have been studied as a function of temperature [137,139,140]. The Seebeck coefficient of polyacetonitrile and of a polymeric Schiff base decreases with increase in temperature, and changes sign. With paracyanogens and polyacrylonitriles this parameter is temperature-independent at first, and then begins to decrease.

The temperature at which the Seebeck coefficient of polyacrylonitrile changes sign varies from 120° to 425° according to the temperature of heat treatment. Thus, the conductivity type of semiconducting polymers at a given temperature can be varied. The current carriers are fully or partly degenerate, so that their concentration is not a function of temperature, and carrier mobility is the only factor which determines the change in electrical conduc-

¶ 1 S m$^{-1}$ = 0.01 $\Omega^{-1}$ cm$^{-1}$, in accordance with the SI international system of units [However, British Standard 3763: 1964, "The International System (SI) Units" does not give a unit of conductivity. S is the abbreviation for Siemens (≡ A/V) and is the Continental term for the mho, or reciprocal ohm (Ed. of Translation).]

† 1 aJ = $10^{-18}$ J = 6.25 eV, or 1 eV = 0.16 aJ, in accordance with the SI international system of units.

‡ With the exception of the specimen heated at 730°, whose Seebeck coefficient, however, is extremely small (+0.7 $\mu$V deg$^{-1}$).

tivity of the polymers with temperature. The plot of the Seebeck coefficient of the polymers against the logarithm of their electrical conductivity does not agree with theory, because no allowance is made for the variation of carrier mobility with temperature of heat treatment.

Polymeric chloropyridine ($\sigma_{27°} = 10$ μS m$^{-1}$, $\Delta E =$ = 0.128 aJ)[95], and the polymeric condensation products of 2,6-lutidine with aromatic dialdehydes ($\sigma_{20°} = 30$ nS m$^{-1}$)[61], have a fairly high electrical conductivity despite the fact that their structure is not cyclic. Aniline black should also be regarded as an organic semiconductor. The high conductivity of the material before alcohol-extraction is almost certainly due to impurities. However, the purified hydrochloride of aniline black is also electrically conducting ($\sigma_{27°} = 1$ mS m$^{-1}$; $\Delta E = 0.027$ aJ). Hydrochlorides have a significantly higher electrical conductivity than their bases[105]. We believe this to be due to the formation of ordered structures within the solid polymer: the number of such structures increases when the hydrochlorides are formed, because of the ionic bonds $N^+Cl^-$. When current is passed through the products of the oxidation of aromatic amines by sulphuric acid, an electromotive force is generated[65]. It is probably connected with the presence of ionised sulphonate groups in the polymers (sulphur content 3.83–16.23%). Materials of this type may find application in electrical storage cells[43].

We have seen that the most electrically conducting polymers with conjugated bonds contain nitrogen. This is not fortuitous: the presence of atoms whose outer electrons are relatively weakly bound lowers the activation energy and therefore facilitates the transfer of electrons to localised levels or to the conduction band[129].

The second group of polymers consists of those with linear or slightly branched structures, and having lower electrical conductivities (10 nS m$^{-1}$–10 fS m$^{-1}$). It includes, first of all, the polyvinylenes formed by thermal degradation of poly(vinyl bromide)[43], by dehydrochlorination of poly(vinyl chloride) by sodium pentyl oxide[40] or ultraviolet irradiation[31,32], and also the polymers of acetylene[11,12]. The electrical conductivity of these compounds is rapidly and appreciably decreased by the action of oxygen, from which they can never be completely freed. We include in this group the polyazines ($\sigma_{20°} = 0.1$ nS m$^{-1}$–0.1 fS m$^{-1}$; $\Delta E = 0.26$–$0.45$ aJ)[59], and the polymer of the malonodinitrile ($\sigma_{20°} = 2.3$ nS m$^{-1}$; $\Delta E = 0.163$ aJ)[76].

Tal'roze and coworkers[141,142] have measured the electrical conductivity at 20–80° of a large number of polymers with conjugated bonds — poly(phenylacetylene), its copolymers with hexene and *p*-diethynylbenzene, polyphenylene, poly(azophenylene)s, poly(aminoquinone)s — and have shown that $\Delta E$ varies linearly with $\log \sigma_0$ for all the polymers, in spite of large differences in $\sigma_0$ (0.1 nS m$^{-1}$–$10^{10}$ TS m$^{-1}$) and $\Delta E$ (0.035–0.35 aJ). By analogy with known phenomena in chemical kinetics, this behaviour has been called the "compensation effect"[142]. All the polymers with broad EPR spectral lines were found to have a lower $\Delta E$ than required by the compensation effect, whence it was concluded that a correlation exists in general "not between the electrical conductivity and the EPR spectrum, but between the pseudoferromagnetic properties of the organic structures and their electrical conductivity"[142]. Since only the "pseudoferromagnetic" polymers definitely contained metal atoms, whereas the others were only assumed to contain such atoms, it would be more correct to speak of an increase in the electrical conductivity of polymers containing metals.

In polymers of the first group[71,135] the value of $\Delta E$ decreases with increase in $\sigma_0$, *i. e.* a compensation effect is not observed in general. It has been assumed[143] that this behaviour is common to all polymers with high electrical conductivity.

The electrical conductivity of poly-*p*-diethynylbenzene also does not exhibit the compensation effect[28], although $\sigma_{20°} = 0.1$–1 nS m$^{-1}$. Furthermore, the compensation effects occurs in typical polymeric dielectrics — such as polyethyleneterephthalate — when their electrical conductivity is lowered by increasing their degree of crystallinity[144]. The relationship $E = A + B \log \sigma_0$ holds for dielectrics as well as for polymers with conjugated bonds. The constant $A$ takes the value 0.147 aJ and 0.106 aJ in the two cases respectively; $B = 0.5$ aJ in both cases. It seems clear that the compensation effect is characteristic only of polymers having a sufficiently high energy of intermolecular electronic transitions, but no explanation of this has as yet been given.

The introduction of methylene groups between the benzene rings of the polymer molecule causes a large decrease in the electrical conductivity of poly(azophenylene) and even polytriazene[84]. However, poly(azophenylene) "separated" by two methylene groups retains its high electrical conductivity[84,145]. According to Dulov *et al.*[145], the presence of one methylene group in the monomer unit of the polymer should also increase the conductivity, due to the denser molecular packings as compared with poly(azophenylene), which should facilitate intermolecular electronic transitions. The flexibility contributed by $-CH_2-$ groups permits close packing of the macromolecules. In the presence of two consecutive groups, however, the disturbance of the conjugation should predominate, and the electrical conductivity should decrease. The close juxtaposition of the polymer molecules probably accounts for the slight effect of thermal treatment upon its electrical conductivity: heat treatment of poly(azophenylene), on the other hand, causes a large increase in conductivity.

The electrical conductivity of poly-*p*-diethynylbenzene also increases when the material is heated in a stream of nitrogen[18] to 400–500° and 600°. Ultraviolet irradiation of the polymer after heating to 220° produces a large increase in conductivity, but after a 400° treatment the effect of irradiation is small, and after a 500° treatment the effect disappears.

The polymeric condensation products of polyhydric phenols with aromatic acid anhydrides have semiconducting properties[97]. Their electrical conductivity covers a large range of values. It depends on the nature of the constituents of the polymer, and increases with increase in polymerisation temperature (256–306°) and in compacting pressure (up to 0.98 GN m$^{-2}$). It usually lies between 1 and 100 μS m$^{-1}$, but in certain polymers it can reach 3 mS m$^{-1}$. Measurements of carrier concentration at -196° gave a value of $n = 10^{15}$ cm$^{-3}$. These polymers conduct mainly by positive holes.

Dyes. The semiconducting properties of phthalocyanines were discovered[146,147] in 1948. These would appear to be the earliest investigations of the electrical properties of compounds with conjugated double bonds. Subsequently, semiconductor properties were shown to be present also in diphenylpicrylhydrazyl[147] ($\Delta E = 0.04$ aJ), dyes of various classes[148,149] ($\Delta E = 0.16$–$0.36$ aJ), and blood pigments[150,151]. As in the case of polynuclear hydrocarbons, the width of the forbidden gap ($\Delta E$) depends on

the purity of the material and on the atmosphere in which the measurements are conducted (see Table). The slight increase in the activation energy of phthalocyanine in oxygen is due to surface oxidation, which increases the height of the energy barriers between microcrystallites.

The dark conductivity of phthalocyanines at room temperature is less than 0.1 nS $m^{-1}$.

Semiconducting dyes show appreciable photoconductivity[154]. As in the case of the dark conductivity, the magnitude of the photocurrent increases in an oxygen atmosphere and on raising the temperature. The activation energy attending photoconduction in these dyes is[152] 0.06–0.10 aJ, which is not very different from the energy of singlet–singlet transition[155]. On the other hand, the photocurrent in basic dyes (with the exception of Trypaflavine) decreases in an atmosphere of oxygen or water vapour[156].

The sign of the current carriers in semiconducting dyes were determined by a variety of methods[156,157]. Electronic conduction was found in di- and tri-phenylmethane dyes, and in some xanthene and cyanine dyes; the conduction in the other dyes, including phthalocyanines, was by positive holes. Yet the Hall constant of "metal-free" phthalocyanine is negative[153]. The carrier density (obviously, electrons) in this material is $10^6$–$10^7$ $cm^{-3}$.

Since the crystal contained 0.02–0.2% of copper, one is forced to the conclusion that metal impurities are practically without effect on the electrical conductivity of phthalocyanine.

The mechanism of conduction in organic dyes involves electron capture at localised energy levels, from which the electrons can be emitted into the conduction band (or recombine with holes in the case of *p*-type conduction)[156].

## VI. ABSORPTION SPECTRA

The absorption spectra of dyes have been studied and described in great detail[8]. We shall therefore confine our discussion to the absorption spectra of polymers with conjugated double bonds.

The infrared spectrum of polyvinylene, prepared by treating poly(vinyl chloride) with potassium amide, contains bands which are typical of *trans*-vinylene groups,

TABLE. Semiconductor properties of porphyrin compounds.

| Compound | Temperature range, °K | $\Delta E$, aJ | | Reference |
|---|---|---|---|---|
| | | *in vacuo* | in oxygen | |
| Phthalocyanine | 273–373 | 0.139 | 0.142 | 146 |
| | 373–773 | — | 0.38 | 147 |
| | 423–623 | 0.24 | — | 147 |
| Phthalocyanine under 7.85 MN $m^{-2}$ pressure | 398–543 | — | 0.13 | 147 |
| | 543–673 | — | 0.18 | 147 |
| α-Phthalocyanine | 323–443 | 0.04 | — | 116 |
| β-Phthalocyanine | 573–673 | 0.14 | — | 116 |
| Phthalocyanine | 293–473 | 0.27 | 0.30 | 152 |
| | — | 0.27 | — | 153 |
| Sulphonated phthalocyanine | 273–373 | 0.144 | 0.147 | 146 |
| Hematin | 345–403 | 0.29 | — | 149 |
| | 123 | 0.325 | 0.325 | 151 |
| Hemoglobin | 373–423 | 0.44 | — | 150 |
| Globin | 373–423 | 0.475 | — | 150 |
| Hematoporphyrin | — | 0.331 | 0.336 | 151 |
| Protoporphyrin | — | 0.29 | — | 151 |

and also a weak band at 1170–1150 $cm^{-1}$, corresponding to oxygen bridges between the macromolecules[158]. This band is drastically suppressed by oxidation of the polymer: at the same time, typical bands for the OH and C=O groups appear, and a strong absorption (due to the formation of a network of C–C– and C–O–C bonds) is observed in the region 1000–1300 $cm^{-1}$. A strong absorption at ~1300 $cm^{-1}$ occurs also in the polymeric condensation product of acetaldehyde[50], in poly(azophenylene), and in poly(phenylacetylene)[159]. With the latter polymer the background absorption increases as the depth of colour of the material increases, the characteristic bands in the 700–1800 $cm^{-1}$ region decreasing in intensity at the same time. In the infrared spectra of the copolymers of poly(azophenylene) with *p*-diethynylbenzene, and also in those of poly-*p*-diethynylbenzene, the characteristic absorption bands are either very weak or quite unresolved; the background absorption in these spectra is very strong over the whole frequency range[159]. The infrared absorption spectra of other polymers with conjugated bonds show only some well-defined functional groups[53,55,83]. A systematic survey[160] of the infrared spectra of various polymers with conjugated bonds has shown that an appreciable absorption band is always present at 1585 $cm^{-1}$, and is stronger than the 1615 $cm^{-1}$ band. It is due to the appearance of a quinonoid structure in the polymer as a result of conjugation. The introduction of substituents in the benzene rings, and also the presence of intermediate groups such as triazene or methylene groups, decreases the proportion of quinonoid structures in the polymers.

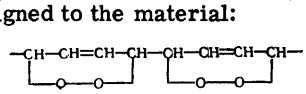
Some bands were also found to correspond to stretching vibrations of the carbon–carbon bonds between benzene rings: these disappear when the system departs from coplanarity. The insoluble polymeric fractions had a stronger background absorption, and less well-defined characteristic absorption bands, than the soluble fractions. This can be attributed to the strong intermolecular interaction between conjugated polymer chains. The strong background absorption of three-dimensional polymers with an extended system of conjugation was again confirmed.

Absorption spectra in the visible region were obtained only with irradiated poly(vinyl chloride)[33]. Under the influence of fast electrons (whether in vacuum or in air) a colourless film of the material develops a green colour with an absorption maximum in the region 580–700 nm. At the same time, an absorption peak develops at 420–460 nm, its intensity depending on the integral dose of radiation. When irradiated poly(vinyl chloride) is kept in a vacuum, the absorption curve shifts towards the visible region without changing shape; the transmission coefficient of the film initially decreases at $\lambda > 560$ nm, and then begins to increase in the region of 500–760 nm. There are no definite conclusions regarding the origin of these phenomena.

## VII. REACTIVITY

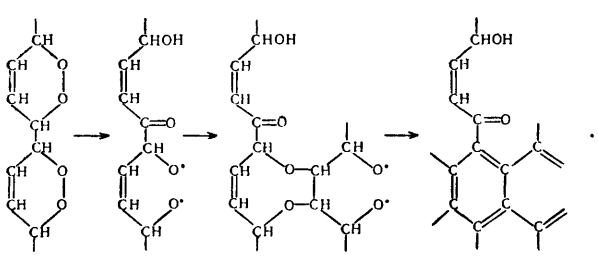
**Polymers with conjugated double bonds.** As a rule, high-molecular polymerisation products with conjugated double bonds do not show a pronounced tendency to react chemically: they are stable towards atmospheric oxygen at 200–250°, and [polyphenylenes and poly(oxyphenylene)s] even up to 400°.[161] Other oxidising agents are also without effect. Poly(aminoquinone)s have a tendency to form chelates with copper and other metallic salts, but this specific property can be ascribed[53,55] to the presence of the >NH group.

Polymers of the polyvinylene type occupy a unique position. Polyacetylenes are easily oxidised by benzoyl hydroperoxide; the resulting peroxide is hydrolysed and oxidised by lead tetraacetate to carboxylic acids[10]. Chlorination of the polymers gives a white insoluble product containing 40% of chlorine[14]. The product of full dehydrochlorination of poly(vinyl chloride) is easily oxidised in the air[39,40], changing from black to light yellow. Meanwhile, its oxygen content increases, the composition changing from $CH_{1.12}O_{0.11}$ before oxidation[41] to $CH_{1.12}O_{0.4}$. According to the degree of dehydrochlorination (0.63–92.91%), the amount of oxygen absorbed varies[162] from 1.65 to 30.32%. It has been stated[40] that oxidised polyene contains up to 32.5% of bound oxygen as well as double bonds; in view of the *trans*-configuration of neighbouring vinylene groups, the 1,4-peroxide structure is assigned to the material:



Oxidation of the polymer obtained from poly(vinylidene chloride) proceeds in a similar way. In every case oxidation causes the loss of the EPR signal and lowers the conductivity of the polymers.

The compound between polyvinylene and oxygen is fairly stable, since it does not decompose in air, but it shows a loss in weight at 150° and above[40]. Boiling 30% nitric acid partly dissolves the product, with formation of oxalic acid and carbon dioxide. The oxidised polymer does not react with potassium iodide, and does not respond to any test for peroxide[162]. When heated in vacuum at 200°, the product gives $CO_2$, water, alcohols, and phenols, with loss of 50% of the bound oxygen; the resulting new polymer is stable to oxidation at high temperatures and gives an EPR signal, and its conductivity is higher by two orders of magnitude[40]. Its melting range[41] is 400–410°. It is suggested[163] that when the peroxide is heated in the absence of oxygen, rupture of the peroxide bridges takes place, followed by polymeric condensation and formation of aromatic structures by partial degradation of the polymer:



The peroxide of polyvinylene oxidises tetralin to decalin[40] at 150° in an inert atmosphere. It can induce the polymerisation of methyl methacrylate even at concentrations of 0.1–0.5 wt.% in the monomer[162].

No significant oxygen affinity could be detected in poly(phenylacetylene), yet it is formed in higher yield in air than in an inert gas[19]. It does not react with maleic anhydride and, like polyacetylene, it is sluggishly hydrogenated by Raney nickel supported on alumina[10]. However, the properties of the polymer are dramatically changed by heat treatment at 300–400° in oxygen or argon: the material darkens and becomes black, it becomes insoluble in acetone and stable to oxidation at 200–300°, its EPR signal increases, and it develops static paramagnetism (the polymer prepared at 150° is diamagnetic). The reaction between poly(phenylacetylene) and *p*-diethynylbenzene at 150° gives a black, insoluble polymer having a three-dimensional structure, as in the case of phenylacetylene[19]. This type of copolymerisation has been called[164] "quasi-radical block copolymerisation"; it appears to occur exclusively with polymers having conjugated bonds. The radiation-induced polymerisation of phenylacetylene is also unusual[26]: its rate is proportional to the integral dose of radiation between wide limits, is independent of dose rate, and is relatively insensitive to temperature ($E$ = 0.005 aJ). The activation energy for initiation is zero. Lastly, poly(phenylacetylene) inhibits the degradation of poly(vinyl chloride)[165] by thermal oxidation at 175–195°, in the same way as (but much more effectively than) compounds which readily yield free radicals. Polyvinylenes have a weaker inhibition effect: at 195–200° they accelerate the degradation of the polymer rather than inhibit it[166]. Polyphenylenes and poly(azophenylene)s do not show an inhibition effect at 175°: the effect appears only[163] at 195–200°.

All four polymers decrease the photochemical aftereffect of the oxidative degradation of poly(vinyl chloride) (leading to the formation of regions with conjugated double bonds and, ultimately, to a polymer of the polyvinylene type).

All the properties listed above justify the conclusion that polyvinylenes, polyphenylenes, and poly(azophenylene)s are free radicals whose relative stability arises from their large size and the strong delocalisation of the free electrons in the macromolecule: they have been termed radicaloids[80,163]. The additional withdrawal of the $\pi$ electrons by the side-chains of benzene rings explains the higher stability of poly(arylacetylene) radicaloids as compared with polyvinylene. The radicaloids become activated at 200–250°, and undergo "quasi-radical" polymerisation and copolymerisation. The radicaloids combine with oxygen, and thus inhibit the degradation of poly(vinyl chloride), but at some stage in the process they become oxygen carriers and begin to accelerate the degradation.

The higher yield of polymer in oxygen is probably also due to the formation of intermediate, very active compounds between the radicaloid and oxygen: this type of "oxygen activation" has also been observed during the radiation-induced polymerisation of phenylacetylene[23], but its activating effect is much smaller than that of radiation.

The small degree of polymerisation of acetylene hydrocarbons is explained by the process of chain propagation through the monomer, which is peculiar to these materials, giving rise to R–C≡C$^{\bullet}$ (M$^{\bullet}$) radicals which do not regenerate the chain and disappear.

This "autoinhibition" mechanism is equally applicable to radiation polymerisation and to thermal polymerisation, initiated by benzoyl peroxide[167,168]. It can be described by the following kinetic schemes:

| Type of process | Radiation polymerisation | Polymerisation initiated by benzoyl peroxide (B) |
|---|---|---|
| Chain generation | $M \xrightarrow{k_0} 2R^{\bullet}$ | $M + B \xrightarrow{k_0} R^{\bullet} + B^{\bullet}$ |
| Chain growth | $R^{\bullet} + M \xrightarrow{k_1} R^{\bullet}$ | $R^{\bullet} + M \xrightarrow{k_1} R^{\bullet}$ |
| Chain propagation and breaking | $R^{\bullet} + M \xrightarrow{k_2} RH + M^{\bullet}$ | $R^{\bullet} + M \xrightarrow{k_2} RH + M^{\bullet}$<br>$B^{\bullet} + M \xrightarrow{k_3} BH + M^{\bullet}$ |
| Recombination | $M^{\bullet} + M \xrightarrow{k_3} D$ | $M^{\bullet} + M \xrightarrow{k_4} D$ |

The rates of radiation and thermal polymerisation, $W_R$ and $W_T$, are given by the expressions

$$W_R = \left(3 + \frac{2k_1}{k_2}\right) k_0 I [M],$$

$$W_T = \left(2 + \frac{k_1}{k_2}\right) k_0 [M][B],$$

and are therefore proportional to the dose of radiation or to the concentration of initiator. The value of $k_1/k_2$ is the same in both cases (3.5–4.0).

Polyazines[59] differ from poly(azophenylene)s in being much less stable at high temperatures; they all melt or decompose at 210–270°. Poly(azinoglyoxal) decomposes explosively, losing 67.5% of its original weight, with evolution of nitrogen, hydrogen, amines, and hydrocarbons. The solid residue is infusible and has a much higher electrical conductivity, and is therefore thought to consist of polyvinylene:

$$(=CH-CH=N-N=)_x \longrightarrow xN_2 + (-CH=CH-)_x.$$

The low thermal stability of polyazine stems from the large number of azo-groups and of partially aliphatic groups in the chain, instead of aromatic groups.

In contrast to the low-molecular polyazophenylenes with $CH_2$ groups in the conjugated chain[84], poly(phenylmethylene)s, produced by different methods[87-99], have a molecular weight $M > 20\,000$, and do not show any "quasi-radical" properties. Relatively low molecular weights ($M$ = 1000–1300) are found in certain poly(naphthylmethylene)s; it is significant that the material with the highest molecular weight ($M$ = 5800) proved to be diamagnetic[93].

The direct reaction of poly(phenylacetylene)s, polyphenylenes, and poly(azophenylene)s with diphenylpicrylhydrazyl (DPPH) suppresses the EPR signal of the latter without affecting the signal of the polymer[169]. The reaction of the first order with respect to the polymer, second order with respect to DPPH, and its product is[170] DPPH-H. The hydrogen is extracted from a molecule of the polymer. The process is induced by paramagnetic centres, which do not themselves participate in the reaction. The fact that the EPR signal of polycyclopentadiene does not change when the material is allowed to stand for 24 h in a solution of 2,4,6-t-butylphenoxyl in a nitrogen atmosphere[107] may be a phenomenon of the same type (but the final concentration of 2,4,6-t-butylphenoxyl was not evaluated).

Polymerisation by the "quasi-radical" mechanism produces three-dimensional high-molecular polymers. Their insolubility in organic solvents, and their stability towards oxidative thermal degradation, in conjunction with their high concentration of unpaired electrons and their static paramagnetism, suggest that the cyclic structure of these materials has the form of a network of aromatic rings which is typical of carbon blacks and coals. The great practical importance of "quasi-radical" reactions by polymers with conjugated double bonds will undoubtedly stimulate further work in this field.

By analogy with inorganic semiconductors, certain polymers with conjugated double bonds may be expected to show catalytic activity, since they are organic semiconductors. The decomposition of hydrogen peroxide is, in fact, accelerated by the presence of aniline black[105], poly(aminoquinone)s[171], and polyacrylonitrile[73]. In the first two cases, the catalytic activity can hardly be ascribed to the organic structure itself, particularly since these polymers have a wide EPR signal and the activity of aniline black decreases with decrease in the chromium content. Furthermore, hydrogen peroxide is extremely sensitive to the catalytic effect of a great variety of solids, and it is difficult to relate these results uniquely to the electronic properties of organic semiconductors[172].

The oxidation of formic acid on polyacrylonitrile[172], whose catalytic activity reaches a steady-state value only after four consecutive experiments, gave more revealing results. The decomposition goes preferentially in the direction of formation of hydrogen. A polymer containing 0.01% of copper(II) chloride is slightly more active ($E$ = = 0.148 aJ; for the copper-free polymer $E$ = 0.176 aJ). Polyacrylonitrile does not catalyse the decomposition of alcohols or the hydrogenation of ethylene.

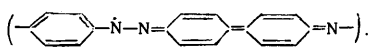
There are some data on the catalytic properties of polyvinylenes. Thus, the polymer of 2-chlorovinyl methyl ketone, when heated to 400° at 1600 N m$^{-2}$, catalyses the oxidation of toluene by air at 380° as effectively as activated carbon with a surface area 2000 times greater[47]. The oxidation proceeds much more smoothly than on transition metal oxides. Again, the polymer containing iron(III) chloride added as an initiator was found to be much more active than the "metal-free" polymer. The same product heated to 1000°, and poly-*p*-diethynylbenzene, heated to 500° or 600° (all in a nitrogen atmosphere), accelerate the conversion[173] of *o*-$H_2$ into *p*-$H_2$. It has been suggested that the active regions of the surface of these polymers can be identified with paramagnetic centres, also the catalytic activity does not vary symbathically with the paramagnetism of the material: only the least active catalyst (poly-*p*-diethynylbenzene heated to 500°) gives an EPR signal. The polymer heated to 600° catalyses the decomposition of formic acid. This property has also been observed in polyvinylene prepared with potassium amide[174] and having the composition $CH_{0.68}N_{0.13}O_{0.14}$. However, the two sets of phenomena are radically different. Hydrogen is sorbed on poly-*p*-diethynylbenzene slowly and weakly, but it is chemisorbed on polyvinylene, which gradually decreases the reaction rate. The chemisorbed hydrogen is only partly removed at 400°. Polyvinylene catalyses also the dehydrogenation of propan-2-ol and the decomposition of hydrazine into nitrogen and ammonia; these processes as well are characterised by considerable sorption (of hydrogen in the former case, and of ammonia and hydrazine in the latter)[174]. As regards the decomposition of hydrazine, it is difficult to speak of a catalytic effect of the polymer, since the reaction occurs above 250°, and both the homogeneous decomposition and the reaction at the glass walls become significant at these temperatures. This is also true of the effect on polyacrylonitrile[172]. The catalytic properties of polyvinylenes can be explained in terms of the formation of intermediate addition compounds at the double bond. However, polyvinylene prepared in an inert atmosphere does not catalyse the oxidation of alkylbenzenes[134] and of carbon monoxide[174], whereas polyvinylene prepared by heating poly(vinyl chloride) in air at 400° (and probably having a condensed structure) is a powerful catalyst for the oxidation of cumene and ethylbenzene[134]. Oxygen addition is probably responsible, giving compounds even less stable than peroxides.

## VIII. THEORY

The theory underlying the properties of compounds with conjugated double bonds presents a difficult problem, which has not yet been finally resolved. Qualitative ideas on the

fundamental role of $\pi$ electrons free to move along the entire length of the conjugated chain [1-3], although correct, are obviously inadequate: they cannot explain, for example, why the number of unpaired electrons is always less than the number of molecules and yet the diamagnetic fractions in certain polymers [163] amount to 90%.

Some discussion is needed of the possibility of $\pi$ conjugation in polymers containing benzene rings separated by $-CH_2-$ groups. It has a low probability, since the $\pi$ electron has to overcome an energy barrier of 0.96-1.12 aJ. It has been shown [175] that spin exchange occurs in the dibenzyl anion, preventing isomerisation with formation of a conjugated chain [176]. However, anion-radicals, which are equilibrium species with one unpaired electron per molecule, and solid polymers, consisting of macromolecules which are diamagnetic in their ground state, are hardly comparable. Polyphenylmethylenes are colourless, have a high molecular weight and a low softening point, and show static diamagnetism: thus, they cannot belong to the class of polymers with conjugated double bonds. Statements [84,145] that electron delocalisation occurs in poly(azophenylmethylene)s are incorrect. The EPR signals of these materials, their high electrical conductivity, and other anomalous properties, can be explained merely by the presence of nitrogen atoms with a tendency to form quinonoid groups of the type



The flexibility of macromolecules containing $CH_2$ groups could be a factor contributing to the electrical conductivity of poly(azophenylmethylene)s [145].

We have at the moment three basic hypotheses on the nature of the magnetic and electrical properties of compounds with conjugated double bonds. According to the first of these [120,122], these properties stem from the paramagnetic impurities which are invariably present in compounds of this type. It has also been stated [163] that dyes and polynuclear hydrocarbons should not be treated as monomeric compounds, because their properties depend on the amount of high-molecular product present in the material. This hypothesis is unsatisfactory, because it fails to explain why the high-molecular impurity should be paramagnetic (paramagnetic ion impurities are excluded, because they can be easily removed), nor does it explain why the impurity is so strongly bound to the host material that it sometimes cannot be removed even by repeated purifications, or why the diamagnetic major constituent is prone to "quasi-radical polymerisation"§.

Another hypothesis aims to interpret compounds with conjugated bonds as charge-transfer complexes (c.t.c.), similar to the complexes formed between benzene and iodine, etc. The c.t.c. concept was first extended to polymeric systems by Blyumenfel'd and Benderskii [177], who showed that a donor-acceptor complex is stable as a linear chain with alternating charges. At the same time, the value of the exchange integral increases with the number of conjugated bonds, giving rise effectively to a single molecular orbital. However, the authors ascribe the ionised states in polymers to the existence of "regions of structural order".

§ The assumption of long-lived macro-radicals is refuted by the EPR signal and the "quasi-radical" polymerisation observed in the formation of the primary polymer by an ionic mechanism, and by the failure of poly(cyclopentadiene) to react with tri-t-butylphenoxyl.

These ideas have been developed in greater detail [178]. The electrical and magnetic properties of systems with conjugated bonds are determined by c.t.c., which are formed either between molecules or between conjugated units within a molecule. It is incorrect to ascribe these properties to the proximity of ground and lowest excited states, resulting from the decrease in activation energy accompanying an increase in the length of the conjugated chain, since this mechanism does not operate at any chain length. The preferential formation of c.t.c. between conjugated systems is due to the fact that the distance between the components of the c.t.c. is less than the distance between neutral molecules. When the material is crystallised, the number of polar states is a maximum at the phase boundary, and as a result the number of c.t.c. in crystals is much larger than in solution. Thus, we can think of these complexes as growth dislocations inevitably arising during crystallisation; it follows that the transition from c.t.c. to a neutral state is impossible without considerable rearrangement of the crystal.

The electrical conductivity of systems with conjugated bonds [178] is explained in terms of the dissociation of c.t.c., charge carriers being set free. The motion of conduction electrons in molecular crystals is accompanied by an adiabatic wave of electronic polarisation, leading to a decrease in the intrinsic energy of the electron. The polarisation energy is given by the expression

$$E = -\frac{D}{V_0} K_{nn} \sum_i \frac{f_i}{\epsilon_i^2},$$

where $D$ is a coefficient depending on crystal geometry, $V_0$ the volume of one molecule in the crystal, $K_{nn}$ the coulomb integral for two electrons in the upper filled orbital, $f_i$ the oscillator strength, and $\epsilon_i$ is the energy of the excited states.

The fact that identical activation energies have been observed [155] for the dark conductivity, the photocurrent, and the first singlet state of a number of dyes justifies the suggestion that excitons with an energy of formation equal to the singlet-singlet transition energy can arise in compounds with conjugated bonds. According to Benderskii and Blyumenfel'd [178], exciton formation is possible when the number of c.t.c. exceeds $10^{16}$ cm$^{-3}$. When this happens, the electrical conductivity of conjugated systems can increase as a result of the capture of electrons by localised levels lying above the valence band, accompanying the dissociation of the excitons.

It should be stressed that the exciton conduction mechanism is hardly ever encountered in dyes [129].

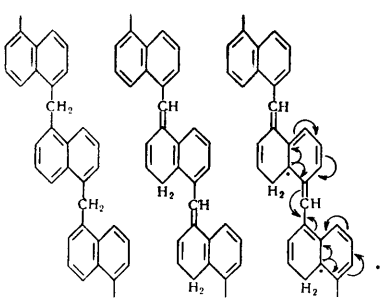
The c.t.c. hypothesis explains also the conductivity of polymers with conjugated bonds. Although the $\pi$ electrons are sufficiently mobile within the macromolecule, electrical conductivity of the material as a whole requires that the electrons cross the potential barrier between macromolecules. This process is made much easier by the existence of intermolecular c.t.c.

The c.t.c. hypothesis is acceptable only for dyes in which the EPR signal is observed exclusively in the solid phase. The increase in strength of the EPR signal of polycyclopentadiene in air can only be explained by the formation of c.t.c. with oxygen, which acts as a charge acceptor. A c.t.c. with oxygen may also be formed at the surface of cyclic polyvinylene [134]; the existence of $O_2^-$ radical-ions as a surface layer on the polymer may be another limiting

case of charge transfer. The reversible increase in EPR signal accompanying decrease in temperature (by Curie's law) is consistent with c.t.c. concepts.

By combining the c.t.c. and the radicaloid hypotheses we arrive at the concept of "local activation" of polymers with conjugated double bonds, according to which high--molecular, paramagnetic polymeric homologues form $\pi$ complexes with the main bulk of the macromolecules, which then activate the system as a whole [163]. The formation of c.t.c. of this type increases the probability of excitation of diamagnetic macromolecules to the biradical state. This model provides a satisfactory explanation of the processes of "quasi-radical" polymerisation and of hydrogen transfer from the polymer of DPPH. The paramagnetism of the high-molecular fractions arises [163] from local unpairing of electrons, and from electron delocalisation along the molecule due to the close proximity of filled and unfilled energy levels. The existence of stable unpaired electrons is made possible by the departure from coplanarity of the conjugated units of the macromolecule.

The hypothesis of electron delocalisation along the whole length of the conjugated chain has not found general acceptance. A theoretical analysis by the molecular orbital method [179] of the "charge density along the bond" in a long polyene chain has given a value of 30% for the delocalisation. The region of delocalisation in the poly(phenylacetylene) anion is confined to two units [180], and the same result was found by analysing the shape of the EPR line of solid poly(phenylacetylene) [181]. Ooshika [182] has reported limited distribution of electrons in an infinitely long chain, and regular alternation of bonds. As a result, he suggests that some particular units in the polymer chain have the nature of free radicals and show appreciable electron delocalisation. In contrast to "structural ordering", these units should be regarded as defects in the polymer chain. The tautomeric forms ascribed [93] to paramagnetic poly-(naphthylmethylene)s are an example of such units:




These "defect sections" are always possible in polyene chains of sufficient length owing to perturbation of the regular alternation of single and double bonds [183]. They can be caused by thermal vibrations, since the energy of formation of the defects is 0.035 aJ. At 300°K they are present in the molecule to the extent of 1.4% by concentration. The defects can move rapidly along the molecule, and become the site of an unpaired electron when they are at a sufficient distance from other similar defects. Defects in the polymer chain can enhance its semiconductivity, since thermally excited electrons are more readily transferred to "defect" orbitals than to the conduction band.

Levich *et al.* [184] state that the conductivity of a polymeric molecule (considered as a one-dimensional conductor with degenerate electrons) is determined by the interactions between electrons and "defects", and is independent of temperature. However, the width of the EPR line is determined by the spin interaction of the electron with the nuclei of atoms in the polymer.

It is not possible at the present time to choose between the hypotheses discussed above. A theory of the properties of compounds with conjugated double bonds which shall be free from contradictions must await new, detailed, and careful investigations.


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