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Conjugated Inorganic Carbon-based Polymers

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Polymers of different types based on dicyanogen, dithiocyanogen, carbon suboxide, and carbon subsulphide, which exhibit conducting or semiconducting properties, are examined. The methods of synthesis, the polymerisation mechanisms, and the chemical and physical properties of these polymers are discussed.
The bibliography includes 192 references.

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I. INTRODUCTION

Wide interest has been manifested in recent years in the study of compounds with electronic properties and of a quasi-one-dimensional or quasi-two-dimensional character. Intense investigation of low-dimensional structures was stimulated by Little's familiar idea[1] of the possibility of creating high-temperature superconductors on their basis. Solids such as charge-transfer complexes (CTC) of the tetracyanoquinodimethane–tetrathiofulvalene type, mixed valence platinum complexes (KCP)† type, $K_2Pt(CN)_4Br_{0.30}\cdot.2.3H_2O$, etc., have since become classical examples of systems which exhibit a whole series of collective phenomena associated with their quasi-one-dimensionality[2]. These phenomena as well as the concepts developed to account for them can be transferred also to certain polymers. With the aid of chemical methods, it is possible to predict the existence of a whole class of materials with extremely remarkable electrical and magnetic properties[2]. Since 1973, polysulphonitride $(SN)_x$, which is the first example of polymers with a metallic conductivity ($\sim 10^3\ \Omega^{-1}\ cm^{-1}$ at room temperature), has been studied vigorously. Furthermore, near 0.3 K there is a transition to the superconducting state; this discovery demonstrated the possibility, in principle, of the existence of superconductivity in a system without metal atoms. Detailed investigations in recent years[3] have shown that $(SN)_x$ is not in fact a one-dimensional system; it would be more correct to regard it as a highly anisotropic solid with a two- or three-dimensional band structure. Indeed, in the case of markedly quasi-one-dimensional complexes (CTC, KCP), a transition to the non-conducting state is observed as the temperature is reduced, while $(SN)_x$ continues to exhibit metallic properties however low the temperature.

According to Ginzburg[4], quasi-two-dimensional systems are more promising in this respect. Thus, following intercalation (the introduction of extraneous molecules into the interplanar spaces), the conductivity of many transition metal dichalcogenides changes from the semiconducting type to metallic and at sufficiently low temperatures these materials become superconductors[5]. Numerous intercalated graphite compounds are also well known[6]. The results of the intercalation of graphite by SbF_5 molecules merit particular attention; the conductivity then increases to $\sim 10^6\ \Omega^{-1}\ cm^{-1}$, exceeding by 60% the conductivity of metallic copper, while the anisotropy of the conductivity becomes greater than 10^6.[7,8] The superconducting transition in potassium-intercalated graphite observed recently[9] stimulated still further the interest in low-dimensional structures.

However, the class of systems investigated has hitherto been restricted in essence to dichalcogenides and graphite. Evidently a specific search in this field is impossible without the accumulation and systematic arrangement of knowledge concerning other low-dimensional systems which have been known for a fairly long time but whose electrophysical properties have either not been investigated at all or have been investigated at random. It is not superfluous to note that $(SN)_x$ was synthesised as early as 1910, but its unique properties remained unknown for more than 60 years. We have written this review in order to draw the attention of investigators to certain polymers which have been known for a long time, but whose investigation can lead to the expansion of our ideas concerning the electronic phenomena in solids.

II. POLYCYANOGENS

A polymeric form of cyanogen was discovered by Gay-Lussac[10] in experiments on the thermal decomposition of $Hg(CN)_2$; dicyanogen $(CN)_2$ was discovered at the same time. The composition of the polymerisation product corresponding to the formula $(CN)_x$ was soon established by Johnston[11,12], who called this polymer "paracyanogen",[12] the name which is still used. Since two polymeric forms of cyanogen are known at the present time, we shall employ this term in relation to only one of these forms.

1. The Paracyanogen Formation Reaction

There exist fairly numerous reactions leading to the formation of paracyanogen, usually as one of the products. Thus the thermolysis of dry noble metal and copper cyanides, which has been the usual preparative method for synthesising dicyanogen since the XIXth century, always leads to the formation of some paracyanogen (see the thorough review of Brotherton and Lynn[13]). Heavy metal cyanamides behave

† Kalium cyanoplatinat.

similarly[14]. Paracyanogen is formed when solid KCN interacts with the vapour of iodocyanogen[15] at the usual temperature; the reaction of chlorine with KCN at 673 K yields paracyanogen as the main product[16]. Paracyanogen arises as a side product in the pyrolysis of α-nitroguanidine,[17] *N,N'*-bis(sulphur trioxide)dicyanogen[18], cyanuric triazide[19], and melaminium hexacyanoferrate(III);[20] it is also obtained when a mixture of KCN and liquid SO_2 is stored for a long time at room temperature[21]. Considerable amounts of paracyanogen are obtained when cyanuric acid amide is acted upon by P_2O_5 [22] and in the reaction of PCl_5 with KCN or $K_4Fe(CN)_6$.[23] Paracyanogen is readily obtained on heating iodocyanogen[24] or cyanuric iodide[25] and in the interaction of CaC_2 with nitrogen[26].

The majority of the syntheses of dicyanogen[13] can apparently be used also to obtain paracyanogen *in situ*, when the reaction is carried out at a sufficiently high temperature and in a closed volume. Apart from the processes already enumerated, one may include among them the heating of dry cyanides in the presence of oxidants ($FeCl_3$, PCl_5, $HgCl_2$, etc.) and the dehydration of ammonium oxalate or oxamide under the influence of P_2O_5 or P_2S_5. Paracyanogen can also be obtained by the electrochemical oxidation of a solution of AgCN in pyridine[27].

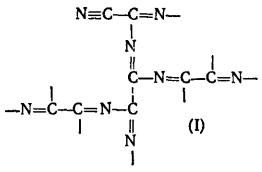
The pyrolysis of mercury and silver cyanide is used for the preparative synthesis of paracyanogen[28-30]. The total decomposition of $Hg(CN)_2$ takes place after 72 h at 623 K, after 26 h at 713 K, and after only several minutes at 873 K; the yield is higher the lower the temperature and the higher the pressure[28,31]. In order to eliminate mercury, a stream of dicyanogen is passed over the preparation at 713 K; the resulting $Hg(CN)_2$ is then distilled off. The yield of paracyanogen from AgCN is 64% at 713 K and a pressure of 6 MPa;[28] silver is removed by treatment with nitric acid. However, it was noted later[30] that the product obtained in this way can in fact consist of a mixture of $(CN)_x$ and $Ag(CN)_x$, the content of $(CN)_x$ by weight being very low. It is possible to obtain paracyanogen by heating oxamide in an evacuated vessel at 543 K; the yield reaches 30–40% when the reaction is carried out for a week and 10% in the course of two days[29]. Paushkin and coworkers[32] suggested that paracyanogen be obtained by heating oxamide or ammonium oxalate in the presence of a large excess of $ZnCl_2$ as the catalyst and dehydrating agent. After 5 h at 673 K, the yield is 30% for oxamide and 14% for the oxalate; according to X-ray diffraction data, the degree of crystallinity of the resulting polymer is high. According to Hittorf[33], the electrolysis of an aqueous KCN solution is a very convenient way of obtaining paracyanogen, giving a quantitative yield of this product. However, other workers[34] believe that this procedure does not yield paracyanogen but the polymer $(HCN)_x$ as a consequence of the hydrolysis of the dicyanogen formed initially to HCNO and HCN and subsequent rapid polymerisation of HCN. Since elemental analyses are not given in either communication, the problem still remains obscure.

Dicyanogen is known to be a chemically reactive compound—it is one of the most reactive nitriles. It is thermodynamically unstable, because its heat of formation is positive (309 kJ mol^{-1}).[13] However, in the absence of moisture and light, pure dicyanogen can be stored indefinitely at room temperature[25]. It has been found[16,31] that at atmospheric pressure and a temperature above 583 K, dicyanogen polymerises to a slight extent; this also occurs at 493 K and pressure up to 30 MPa and paracyanogen is formed even near the critical point, although very slowly[28,31]. However, these results appear to be doubtful. Chromatographically pure dicyanogen heated to 373–1473 K does not polymerise for two weeks[36]. Apparently the results of the above investigations[16,28,31] can be accounted for by the insufficient purity of the dicyanogen employed. The catalytic activity of various substances on the polymerisation of dicyanogen has been investigated. In the presence of K_2CO_3 the polymerisation begins at a temperature as low as 393 K and the same effect is produced by $NaNH_2$, but both salts begin to interact with paracyanogen as the temperature is increased. KCN, which does not react appreciably with paracyanogen, is a good catalyst at 713 K. The surface of glass exhibits only a weak catalytic effect and quartz is even less active[16]. The polymerisation of dicyanogen is catalysed by acids (CH_3COOH, HCN, CO_2), bases (NaOH, Na_2CO_3), traces of moisture and air, and metallic copper[12,35], but surprisingly, platinised asbestos has no effect[37]. When water is saturated with dicyanogen, paracyanogen appears in the solution after the latter has been allowed to stand for a long time[38] and, when dicyanogen is passed through a concentrated KOH solution, paracyanogen is precipitated immediately[38-40].

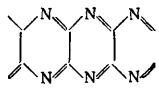
In the absence of impurities, the polymerisation of dicyanogen is induced by ultraviolet irradiation[41-45], an electric discharge[46-48], and α-particles[49-52]. Dicyanogen also polymerises in the presence of active nitrogen[53] and in the ionisation chamber of the mass-spectrometer[54,55]. Furthermore, paracyanogen is formed when gaseous hydrogen cyanide is acted upon by electric discharges[56-60] and on photolysis of carbonyldicyanogen[61,62]. The appearance of a certain amount of paracyanogen has been noted when activated nitrogen was passed over graphite[63] and on γ-irradiation of sealed tubes containing nitrogen and graphite[64].

2. The Structure and Mechanisms of the Formation of Paracyanogen

Sidgwick[65] was the first to suggest that paracyanogen may consist of a three-dimensional system (I) or a cyclic system (II):

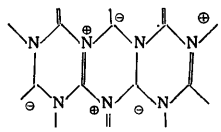


(I)



(II)

It has been established[29] that the infrared spectra of different paracyanogen specimens give rise to only one distinct absorption band at 1570 cm^{-1}, corresponding to a system of conjugated bonds. Having examined several structures, corresponding to linear (four-membered rings), ladder [six-membered condensed rings (II)], and parquet (ten-membered rings) polymers, the investigators selected structure (II). However, it has been justly noted that the band at 1570 cm^{-1} is characteristic of almost all substances containing the C=N bond and, contrary to the belief of Bircumshow et al.[29], provides no information whatever about the structure of paracyanogen. According to Rodewald[66], paracyanogen has a layer lattice of the type of graphite in which each second carbon atom is replaced by a nitrogen atom. The structural unit consists of a triazine and not a pyrazine ring. Thus the structure of paracyanogen can be described by a set of numerous valence structures of type (III) and its dark colour and high stability are due to resonance interactions. The parameters of the hexagonal layer lattice



(III)

a, c, and ρ_{theor}, determined[66] from X-ray measurements, are 0.136 nm, ~0.45 nm, and 2.0 g cm^3 respectively. The difference between the interatomic distances in paracyanogen and graphite is thus small, so that the nitrogen atoms in paracyanogen can be replaced by carbon atoms. As a result, the non-stoichiometric forms of paracyanogen never contain an excess of nitrogen and always contain an excess of carbon (see Section IV). With increase of the carbon content, the X-ray density ρ_{theor} increases, since the decrease of the parameter c is more than compensated by the increase of the parameter a. Similarly, the enthalpy of formation and the thermal and chemical stabilities increase, the colour deepens, and the electrical conductivity increases.

For a long time the attempts at a thermodynamic description of the interconversions in the dicyanogen–paracyanogen system were unsuccessful[28,37,67], because equilibrium is attained only when paracyanogen and not dicyanogen is used as the starting material. Rodewald explained this phenomenon[66]. Although the only product of the decomposition of paracyanogen is dicyanogen, the latter is not an equilibrium phase but constitutes a secondary product. On the other hand, the primary product is monocyanogen CN, which can be formed from paracyanogen as a consequence of the C–N bonds and from dicyanogen as a consequence of the dissociation of the C–C bonds. The enthalpy of the dicyanogen–paracyanogen transition, calculated by Rodewald, is close to 180 kJ. Taking into account the bond enthalpies in dicyanogen, the enthalpy of formation of paracyanogen is ~3.81 kJ. Since the heat of dissociation is 545 kJ mol^{-1}, the formation of paracyanogen never follows the shortest path $(CN)_2 \rightarrow (CN)_x$; an obligatory condition for the condensation of paracyanogen is the formation of monocyanogen: $(CN)_2 \rightleftharpoons CN \rightleftharpoons (CN)_x$. Thus monocyanogen can be converted either into dicyanogen (the formation of new C–C bonds) or into paracyanogen (the formation of C–N bonds). The second pathway is energetically more favourable, but it presupposes a fairly high partial pressure of monocyanogen.

Indeed all the results known to us confirm that Rodewald is right. It has been established[42,43] that the gas-phase photolysis of dicyanogen involves polymerisation and the quantum yield of the reaction is 3 mol einstein^{-1}. Such a low yield rules out a chain polymerisation mechanism. It has been suggested that the dissociation of $(CN)_2$ is followed by the reaction $CN + (CN)_2 \rightarrow (CN)_3$; the latter product is unstable and polymerises to paracyanogen. The thermal polymerisation of dicyanogen also begins[68,69] with the addition of the CN radical to the $(CN)_2$ molecule. These results can be interpreted only in the following way. The nucleophilic attack by the N atom of the highly polar monocyanogen on a C atom of dicyanogen should lead to a "head to tail" type of addition, so that the sequence of atoms CNCN... in the polymer is preserved. It is natural to expect that the $(CN)_3$ radical consists of a triazine ring, i.e. it constitutes the structural unit of paracyanogen#. The ease of formation of paracyanogen from substances containing the triazine ring[19,22,25] may be regarded as an additional argument in support of structure (III).

We may note that the unstable $(CN)_3^-$ ion, arising when the CN^- ion reacts with dicyanogen, has been detected even in an aqueous solution.

The radical mechanism of the formation of $(CN)_x$ is in many instances evident; the reaction proceeds on the wall at a rate limited by the rate of diffusion[20,53,63,71]. The catalytic effect shown on the polymerisation of dicyanogen by a wide variety of compounds or pressure has not so far been explained. One can only postulate that the transition state, in which the C–C bond is weakened, plays a significant role, particularly in the latter case. The doubled yield of paracyanogen[29] from $Hg(CN)_2$ compared with AgCN can possibly be accounted for by the catalytic effect of the HgCN radicals, which exist[72] at ~773 K.

Under the influence of ionising radiation, dicyanogen polymerises via an ionic mechanism[49–51,54,55]; the ions of the inert gases (He, Ne, Ar, Kr, Xe, N_2, and CO_2) then behave as catalysts. It has been noted[49] that Xe is incorporated in the composition of paracyanogen, but can be removed by heating to 623 K.

3. Chemical and Physical Properties of Paracyanogen

Depending on the methods of synthesis, paracyanogen is a powdered or porous substance with a colour ranging from brown to black and is insoluble in the usual solvents (see, for example, Refs. 29 and 52). The product obtained by Paushkin et al.[32] has a high degree of crystallinity. Paracyanogen films are also known[45]. The majority of the chemical properties of paracyanogen have already been described as early as the past century[11,12,28,38]. On heating in the absence of air, the substance begins to decompose to dicyanogen at 773 K. Complete depolymerisation occurs only at 1133 K and in the given range equilibrium is established at each temperature[28,37]; this process is accompanied by some decomposition of dicyanogen into the elements. On heating in a stream of nitrogen, paracyanogen decomposes into NH_3, HCN, and carbon[38] even at low temperatures, while in a stream of chlorine the product is chlorocyanogen[29,38].

Paracyanogen reacts fairly readily with Na_2CO_3, KOH, and soda-lime melts[29,38,73]; the initially brown melt is slowly converted into an orange-red melt and than a colourless melt; NH_3 is evolved and CN^-, CNO^-, and CO_3^{2-} ions are detected in the melt. Dicyanogen is probably an intermediate. Paracyanogen also interacts with $KHSO_4$ melt, giving rise to a substance with a deep red-brown colour. Fusion with potassium converts the polymer into KCN, but there is no reaction with sulphur and phosphorus melts. Paracyanogen does not react with aqueous solutions of alkalies, with ammonia, and with hydrocyanic acid[73], is partly soluble in 60% $HClO_4$ and in concentrated sulphuric and phosphoric acids, and is much less soluble in hydrochloric acid[29]. All these solutions have a deep colour and exhibit an intense pale-blue fluorescence on ultraviolet irradiation. Dilution with water leads to the precipitation of paracyanogen. We may note that these properties are more characteristic of colloidal solutions; the formation of colloids is in fact to be expected for a substance with structure (III).

The addition of a paracyanogen solution in H_2SO_4 to boiling concentrated HNO_3 entails the formation of a pale-yellow solution; the addition of $HgSO_4$ solution to the latter gives rise to a brown cheesy precipitate, which is converted on standing to yellow acicular crystals of "mercury paracyanate" C_4N_4OHg.

"Silver paracyanate" $C_8N_8O_2Ag$ is obtained similarly[12]. When paracyanogen interacts with hydrazine over a period of 20 h, the extent of its degradation is only 20% with formation of dark water-soluble substances[74].

An interesting property of paracyanogen is its ability to adsorb metals whose standard potentials are greater than −0.4 V from dilute aqueous solutions of their salts[75]. Here it

is easy to see an analogy with the behaviour of graphite or transition metal dichalcogenides.

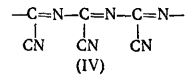
The infrared spectra of various $(CN)_x$ specimens obtained from oxamide, $Hg(CN)_2$, and AgCN contain an intense band at 1570 cm^{-1}, which has been assigned to the conjugation system[29]. After heating in air at 723 K, this band disappears and new bands appear at 640 and 1100 cm^{-1} in the case of oxamide and at 640 and 810 cm^{-1} in the case of $Hg(CN)_2$, which have not been assigned to any particular structure. If the paracyanogen precipitated from a solution in H_2SO_4 with water is redissolved in H_2SO_4, a new band appears in this spectrum at 2070 cm^{-1}, which has been assigned to the CN^- ion[29]. Since in the latter case one is dealing only with low-molecular-weight fractions, the appearance of this band can be accounted for by the protonation of some of the N atoms with subsequent addition of the counterions CN^-, arising as a consequence of the partial decomposition of paracyanogen. These data are contradicted by the results of a study[30] where the 1570 cm^{-1} band was not observed in the spectra of specimens obtained from AgCN. The authors noted an intense absorption at 1400 cm^{-1}; furthermore, the band at 2170 cm^{-1} persisted and a strong diffuse absorption was found at 3000 cm^{-1}. If there is a considerable difference between the degrees of polymerisation of the paracyanogen specimens, then the substituents at the ends of the molecules can exert a strong influence on their symmetry and hence on the relative intensities of the bands. It has been suggested that the product obtained by Wu et al.[30] is a mixture of heterocyclic substances with different degrees of polymerisation.

Measurements of the electrical conductivity of paracyanogen also differ very markedly depending on the method employed; values of 10^{-3}–10^{-4},[76] 1.7×10^{-5},[32] 2.0×10^{-6},[77] and 5×10^{-14} Ω^{-1} cm^{-1} have been obtained[78]. Paracyanogen films ~13 nm thick transmit a current of 50 mA at a field potential of 10^7 V cm^{-1}.[45] Like all polymers with a system of conjugated bonds, paracyanogen is a paramagnetic substance with a spin concentration of 5×10^{17}–1.7×10^{18} spins g^{-1}.[32,79] The study of the nature of the paramagnetic centres led to the conclusion that they consist of free radicals[79]. Measurement of the dependence of the differential thermo-e.m.f. on temperature showed[76] that paracyanogen behaves as a typical semimetal. Its conductivity is virtually independent of temperature within wide limits[32,45]. One should note particularly that measurements of the activation energy for $(CN)_x$ films in two instances yielded a value of zero, while two other measurements gave 0.16 and 0.02 eV;[45] for a disc, the corresponding value is 0.03 eV.[32] This is fully consistent with the current ideas concerning individual coplanar conjugation blocks in macromolecules, along which charged carriers migrate with a very low resistance[74,80–83]. At their ends there is an energy barrier, which the carriers must overcome in order to jump or tunnel to the next section of continuous conjugation.

In the visible region paracyanogen exhibits photoconductivity[84]; the photocurrent decreases sharply with decrease of the degree of illumination even *in vacuo*. Paracyanogen, being a catalyst of the dark oxidation of ascorbic acid, suffers a decrease of catalytic activity in the light[85]; on passing from red to white light and further to the ultraviolet region, its effect is enhanced. The study of the action of γ-rays on paracyanogen showed[86] that a dose up to 5×10^7 J kg^{-1} does not alter its physicochemical properties. However, it has been shown[77] that storage of paracyanogen for three years in the air leads to a decrease of the electrical conductivity to less than 10^{-14} Ω^{-1} cm^{-1} and a band appears in the infrared spectrum at 3220 cm^{-1} which corresponds to absorption by the OH group. Insoluble paracyanogen fractions become fully soluble in concentrated H_2SO_4.

4. Other Polymers

Paracyanogen is not the only polymeric form of cyanogen $(CN)_x$. Not so long ago, the synthesis of a linear form of polycyanogen, which is polycyanoazopolyene (IV), was reported[87]:



(IV)

The polymer was obtained by the anionic polymerisation of dicyanogen in solution in tetrahydrofuran (THF) under the catalytic influence of butyl-lithium, naphthyl-lithium, or monolithiobenzophenone and its molecular weight is in the range 200–500. The proposed structure is consistent with infrared spectroscopic data: the spectrum of the polymer contains intense bands at 2200 cm^{-1} (due to the $-C\equiv N$ groups of the conjugated system) and at 1600 cm^{-1} (due to the $-C=N-$ conjugation chain) and has been confirmed by the results[88] of electrophoretic analysis. Compound (IV) is a dark substance soluble in water and polar organic solvents and, according to potentiometric titration data, is a mono- or di-basic acid depending on the catalyst employed. The EPR spectrum of compound (IV) consists, as for paracyanogen, of a single narrow line corresponding to a spin concentration of ~10^{18} spins g^{-1}. A fine structure is not observed either at 193 K or at high dilutions, which indicate a strong delocalisation of electrons along the conjugation chain. The electrical conductivity measured in discs is close to 10^{-11} Ω^{-1} cm^{-1} at room temperature and the activation energy is ~1.9 eV.

The polymerisation of dicyanogen under the influence of electric discharges leads to polymers whose composition depends on the experimental conditions[46] and can be described by the general formula $(CN_{1-y})_x$, where $y < 1$. According to other data[48], the polymer $(C_2N)_x$, whose composition is independent of the conditions of synthesis, arises under similar conditions; the reaction is of zero order with respect to dicyanogen and the polymer. The available information about the thermal and chemical stabilities of polymers is just as contradictory[46,48]. Products with the composition $(CN_{0.9})_x$ have also been obtained in the polymerisation of dicyanogen induced by α-particles[49,50].

The pyrolysis of the tetraiodo-derivative of imidazole $C_3N_2I_4$ at 453 K entails a partial elimination of iodine and the formation of a brown polymer $(C_3N_2I)_x$; the residual iodine is split off only at 723 K, giving rise to a polymer $(C_3N_2)_x$.[73,89] Both polymers are outwardly similar to amorphous carbon. After prolonged heating, the colour changes to dark grey and the substances are converted into hard graphite-like grains. The chemical properties of $(C_3N_2)_x$ resemble those of paracyanogen[73] and on heating the polymer decomposes in accordance with the equation $(C_3N_2)_x \rightarrow (CN_2) + C$. It was established later[90] that the pyrolysis of $C_3N_2I_4$ at 723 K gives rise to a product with the ratio C : N = 1.7 still containing 0.37% of iodine. The conductivity of this polymer is 10^{-9} Ω^{-1} cm^{-1}. An increase of the pyrolysis temperature to 973 or 1073 K increases the ratio C : N from 3.2 to 6.2 and the conductivity to 2.5×10^{-2} and 0.5 Ω^{-1} cm^{-1} respectively. Triiodoimidazole behaves similarly.

Black graphite-like compounds with the compositions $(C_4HNI)_x$, $(C_4HN)_x$, $(C_4IS)_x$, and $(C_4S)_x$ have also been obtained[89] (see also Ref. 91 and 92).

It is natural to suppose that polymers of the type $(CN_{1-y})_x$ have the graphite crystal lattice and can be regarded as "copolymers" of graphite and paracyanogen. After prolonged heating, $y \rightarrow 0$, which leads to an increase of entropy and the residue consists of cryptocrystalline graphite. It

appears likely that the I atoms do not enter directly into the $(C_3N_2I)_x$ lattice but are located in the interplanar spaces, which is usual for layer compounds.

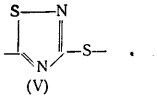
The polymerisation of dicyanogen in the presence of dry ammonia[93] or an aqueous solution of cyanide and weak acids[94,95] leads to the formation of black polymers soluble only in concentrated H_2SO_4 and decomposing at 1123–1173 K with evolution of $(CN)_2$ and HCN. Their structure has not been established. The polymers have a high heat of combustion and can be used as solid rocket fuel. Yet another cyano-polymer $(CN_4)_x$ is obtained[96] in the spontaneous polymerisation of cyanazide N_3CN; when the polymer comes into contact with water, HN_3 is evolved.

III. PARATHIOCYANOGEN

Dithiocyanogen $(SCN)_2$ was first obtained in a free state by Söderbäck[97], who established that, on rapid heating, this compound is converted, sometimes explosively, into the brick-red parathiocyanogen $(SCN)_x$. Small drops and thin layers of dithiocyanogen gradually solidify, forming a transparent brick-red resin. It was later established[98] that sufficiently pure dithiocyanogen, which melts near 298 K, polymerises on rapid heating without explosion. Boron halides catalyse the polymerisation[21]. Parathiocyanogen is one of the products of the decomposition of nitrosylthiocyanogen[21,98] and cyanazide dithiocarbonate[99], and is formed on dry heating $Hg(CN)_2$ with metal sulphides[100] and on interaction of $SOCl_2$ with AgSCN.[101] Melts of thiocyanates are readily oxidised by $FeCl_3$, $K_3Fe(SCN)_6$, $CuCl_2$, $Co(NH_3)_6Cl$, $Cu(SCN)_2$, and K_2SnCl_6, giving rise to parathiocyanogen and dithiocyanogen, which rapidly polymerise in the presence of ammonia[102]. Parathiocyanogen can be obtained also as the product of the electrochemical oxidation of melts[103–106] or solutions of thiocyanates in dimethyl sulphoxide[107]. The interaction of iodine either with melts[108] or with aqueous solutions of thiocyanates[109] is apparently the most convenient method of synthesising parathiocyanogen.

Solutions of dithiocyanogen in organic solvents are stable only at low temperatures and in the dark; on heating or ultraviolet irradiation, they precipitate a deposit of parathiocyanogen[110]. Concentrated solutions of NH_4SCN behave in the same way in the light[111,112]. It appears that in all cases one must put forward a radical mechanism of the polymerisation of dithiocyanogen. The ease of the dissociation of the S–S bond is evident; the first stage in the formation of $(SCN)_x$ from the other compounds considered is the production of SCN radicals, which rapidly and irreversibly polymerise. This is confirmed also by measurements of the magnetic susceptibility of solutions of $(SCN)_2$ by Gouy's method. It has been established[113] that freshly prepared 0.5 *N* solutions in CS_2 and $CHBr_3$ are diamagnetic. After prolonged standing, the solution in CS_2 acquires a yellow colour and becomes paramagnetic; in cyclohexane the paramagnetism appears immediately.

The structure of parathiocyanogen has not been established. Söderbäck[114] proposed the following structure (V):



(V)

However, it is known[102] that the infrared spectra of $(SCN)_x$ contain bands at 2070–2080 and 1600 cm^{-1}. The first is characteristic of organic thiocyanates and isothiocyanates and the second can be assigned to conjugated –C=N– bonds. Evidently structure (V) does not agree too well with these results. We suggest that the linear structure (VI) is more probable:



(VI) (VII)

It has been shown[105] that electrodes coated by a film of parathiocyanogen become photoactive (for example, the reduction of Cd^{2+} ions at such an electrode is accelerated when the latter is illuminated), the magnitude of the photoeffect depending on the $(SCN)_x$ deposition conditions; ageing of the precipitate leads to a decrease of the photoeffect. It has been suggested[105] that the precipitate contains initially free radicals which undergo complete polymerisation after a time; the fresh precipitate is a semiconductor. Structure (VI), which we proposed, fully explains this behaviour of the precipitate. Indeed, after a time unpaired electrons at the individual carbon atoms can recombine with formation of cross-links. Furthermore, the conductivity band in structure (VI) is 1/6 filled, which agrees with the semiconductor properties. An alternative version is structure (VII).

We may note that dithiocyanogen can be regarded as a member of the homologous series of cyanosulphanes $S_n(CN)_2$, where $n = 1–8$. All cyanosulphanes are stable only at low temperatures, vigorous polymerisation occurring on heating with formation of amorphous glassy red products of unknown structure[115]. It may be that these polymers also contain chains of type (VI).

The chemical properties of parathiocyanogen have been scarcely investigated. It is insoluble in dilute acids and alkalies and in all organic solvents, decomposing above 573 K.[114]

It has been known for a long time[116] that selenocyanogen $(SeCN)_2$ is unstable both in air and in solution. Presumably it also tends to polymerise, like $(SCN)_2$, but there is no information in the literature about its polymers.

IV. CARBON SUBOXIDE POLYMERS

1. The Formation of Polymers and Polymerisation Mechanisms

Carbon suboxide C_3O_2, discovered by Diels and Wolf[117], has a linear structure and is the simplest diketone. In the early investigations it was already noted[117,118] that a characteristic property of the suboxide is a tendency towards polymerisation. A fairly pure preparation is entirely stable at low temperatures and in the dark and even brief contact of its vapour with an incandescent platinum wire does not induce reaction[119]. The polymerisation of C_3O_2 is initiated by traces of moisture and mercury[120], phosphorus oxides[121,122], H_2SO_4, $AlCl_3$, BF_2, organic compounds[123,124], methanol, HCl, and ammonia[125]. Temperature is very important[126,127].

The principal characteristics of the polymerisation of C_3O_2 in the gas phase reduce to the following[128]. The rate of polymerisation increases with increase of temperature and pressure. The polymerisation is preceded by an induction period, the duration of which depends on the temperature but cannot be predicted for any one temperature. The reaction is heterogeneous and the induction period depends strongly on the nature of the surface of the reaction vessel, decreasing sharply if the surface is acidic (for example, in the presence of traces of H_2SO_4 or P_2O_5). If the walls are coated with paraffin, the induction period lasts more than a week. The polymerisation does not require photoinitiation and its course is the same both in the dark and in the light. The polymers obtained at room temperature are yellow, those at 373–573 K are red, and those at 673 K are violet.

Further study of the thermal block polymerisation was carried out by Blake[129], who found that the activation energies for the process are 26 and 34 kJ mol^{-1} in Pyrex and quartz vessels respectively. The duration of the induction period (ranging from minutes to several days) was satisfactorily reproducible, increasing with decrease of temperature and pressure. The reaction is of first order; the addition of CO, CO_2, O_2, NO, and C_2H_4 to the system does not affect the rate of reaction; isobutane causes a slight decrease and CCl_4 a considerable decrease of the rate of reaction and give rise to a deviation from the first order. The rate of reaction depends also on the ratio of the surface of the vessel to its volume. According to Blake[129], the presence of an induction period and the nature of the influence of additives indicate a heterogeneous reaction mechanism; in the gas phase the reaction proceeds without the involvement of free radicals, although the possibility of a surface free radical reaction cannot be ruled out. Thus the presence of the polymer does not influence the rate of reaction§, while the presence of the carbonised polymer increases the rate at low temperatures, which can be attributed to a high concentration of paramagnetic centres ($\sim 10^{20}$ spins g^{-1});[130] these centres can initiate the formation of polymerisation nuclei.

The kinetics of the thermal polymerisation of C_3O_2 subjected to preliminary irradiation by light (253.7 nm) were investigated by Smith[131]. The first order of the reaction with respect to the monomer and the polymer was confirmed, i.e. the reaction is autocatalytic. According to Smith's data, the overall activation energy on a quartz surface is 26.1 kJ mol^{-1}. Yet another confirmation of the first order of the reaction was obtained in an EPR study of the polymerisation kinetics[132,133]; the experimental activation energy in a quartz vessel was 41 kJ mol^{-1}, which is close to Blake's result[129].

The thermal polymerisation of C_3O_2 can be carried out not only in the gas phase but also in non-polar[134–140] or polar[136,141] solvents. The possible mechanism was discussed by Ziegler et al.[37], who assume that the anhydride of 3-oxoglutaric acid is an intermediate, being formed in the interaction of C_3O_2 with malonic acid. Since C_3O_2 is the anhydride of malonic acid, the presence of traces of moisture is evidently required. The use of other initiators can lead to the intermediate formation of a ketencarboxylic acid or its derivatives[125]. Later the authors[142] stated that in this mechanism the high-temperature polymerisation is possible only as an exception. A mechanism involving the initial formation of the dimer $(C_3O_2)_2$, which is an alkylketen, has also been proposed[143]. Next this keten combines in succession with fresh C_3O_2 molecules. However, it has been noted[133] that this mechanism presupposes the formation of polymers with a very high molecular weight, since the reactive alkylketen is formed at each stage, and this conflicts with experimental data.

The most justified mechanism of the thermal polymerisation of C_3O_2 has recently been proposed by Snow et al.[133] The initial stage involves the formation of an activated complex between the bent C_3O_2 molecule and the surface of the polymer or, what is more difficult, the surface of the reaction vessel. Thus the induction period is determined by the probability of the formation of such a complex. Next follows the formation of a zwitter-ionic ketocarbene capable of combining in succession with monomer molecules; the termination stage then occurs via the Wolff rearrangement and the resulting macromolecule contains two ketenyl groups.

§ This is contradicted by early data[120].

The photopolymerisation of C_3O_2 has been described by Bayes[144–146], who investigated the gas-phase photolysis in the presence of ethylene and oxygen. He suggested that, when acted upon by a light quantum, the C_3O_2 molecule gives rise to an active C_2O radical, which is capable of attacking the C=C double bonds and even C–H single bonds. This results in the formation of a polymer, allene, methylacetylene, and CO. There is also a possibility of the existence of two intermediate species with different reactivities[146,147]. In the absence of additives, the photolysis products are only $(C_3O_2)_x$ and CO. It has been established[148] that the photopolymer is analogous to the thermopolymer; the addition of O_2 to the initial monomer reduces the yield of the polymer and for the ratio $O_2 : C_3O_2 = 100 : 1$ the polymer is not formed at all. The eight-stage mechanism of photolysis proposed by Smith et al.[148] includes, apart from the formation of C_2O, the generation of an activated complex C_5O_3 with a structure of diketen-cyclopropanone. It may be[131] that the light-induced thermal polymerisation of C_3O_2 also involves the formation of C_2O.

Ultraviolet irradiation of a solution of C_3O_2 in hexane results in polymerisation[149], which gives rise to a new compound containing a carbonyl group, apparently via the reaction of a hexane molecule with the C_2O radical. Indeed the EPR spectrum of solid C_3O_2 irradiated with ultraviolet light at 77 K has a singlet signal which can be attributed to C_2O. The study of the infrared spectra of the products of the photolysis of C_3O_2 at 100 K confirms the formation of C_2O as the initial species. Next, it was suggested[150] that a tricyclic compound $C_{13}O_8$ is formed, its molecule becoming the polymerisation centres on raising the temperature.

$(C_3O_2)_x$ and CO are also formed in the gas-phase γ-radiolysis of C_3O_2.[151] Since the polymer does not collect on the surface of the reaction vessel as in thermal polymerisation but on its bottom and the addition of O_2 does not influence the yield, an ionic mechanism of the polymerisation reaction, in which the C_2O^+ ions play an important role, is evident. On γ-irradiation, liquid and solid C_3O_2 do not polymerise[152]; on heating the irradiated suboxide from 77 and 180–260 K, the rate of polymerisation is low and on further heating, it rises sharply, reaching a maximum and then falling again owing to the exhaustion of the monomer. The active centres accumulated in the low-temperature radiolysis persist even in liquid C_3O_2, which is attributed to the establishment of steric hindrance which prevents chain termination. The self-acceleration of the isothermal liquid-phase polymerisation in the absence of continuous initiation may be associated with a branched chain reaction. On irradiation of solutions of C_3O_2 in halogeno-hydrocarbons by γ-rays, fast electrons, or ultraviolet light, polymers $(C_3O_2)_x$ with a high molecular weight (>10 000) are formed, temperature and pressure having very little influence on the process kinetics and the properties of the polymers; the use of ether, CO_2, and CS_2 as solvents leads to unsatisfactory results[153]. The polymerisation of C_3O_2 can be induced also by ultrasound[154].

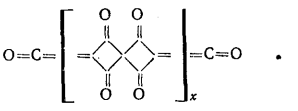
The polymers $(C_3O_2)_x$ are not formed solely from the monomer. It has been known for a long time[155] that, under the influence of a glow discharge, CO is slowly converted into $(C_3O_2)_x$ and CO_2. A thorough study[156] of this reaction showed that the polymer is formed even at 77 K and that the role of C_3O_2 in the formation of $(C_3O_2)_x$ cannot be significant. Analogous conclusions were arrived at also in the study of α-radiolysis[157] and γ-radiolysis[158] of CO; the reaction products were $(C_3O_2)_x$, CO_2, and graphite. The polymer arises from CO also as a result of ultraviolet irradiation or irradiation with fast electrons[160].

There exists a remarkable hypothesis[161], which explains the reddish colour of Mars by the presence of the polymers $(C_3O_2)_x$. Indeed the photolysis and radiolysis of CO lead to the formation of the suboxide, which rapidly polymerises. Many observations of Mars can be explained by assuming the formation of the $(C_3O_2)_x$ species on its surface and in the atmosphere[162]. It is also possible that $(C_3O_2)_x$ is the main component of the clouds of Venus[163].

In conclusion of this Section we may note that the solid red-brown substance obtained by Brodie[164] by exposing CO to the action of silent discharges (long before the work of Diels[117]) was apparently the polymer $(C_3O_2)_x$.

2. Structure and Properties

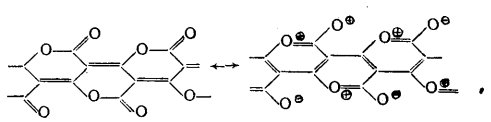
There are at present four hypotheses concerning the structure of $(C_3O_2)_x$ in the literature. The oldest is that of Hartley[165], according to which the polymerisation product is the dimer $(C_3O_2)_2$; its inapplicability from the energetic standpoint is now evident. Somewhat later Diels et al.[134] proposed structure (VIII) on the basis of the analogy between C_3O_2 and ketens. Porejko and coworkers[135,136] arrived at the same structure, justifying it with the aid of classical chemical methods and ultraviolet and infrared spectroscopy:



(VIII)

Having studied the infrared spectra, X-ray diffraction patterns, and chemical properties of $(C_3O_2)_x$, Schmidt and coworkers[138,139] proposed a completely different structure. They believe that the polymer is made up of condensed lactone and benzene rings; oxygen is located mainly in the six-membered lactone rings and at the edges of the molecule (whose diameter is close to 1 nm), there are keto- and keteno-groups. Thus the $(C_3O_2)_x$ lattice is similar to that of graphite, in which some of the C atoms have been replaced by O atoms; the distance between the planes is ~0.36 nm. However, this structure is unacceptable because 15 C_3O_2 units in it are arranged in only one possible way, as a result of which the structure cannot be built up further and less than 15 units cannot be postulated.

In order to construct a reasonable structure of the polymer $(C_3O_2)_x$, it is necessary to take into account the following factors[128]. The polymer must be formed as a result of a reaction involving C_3O_2 as the structural unit. The dimensions of the structure can be varied; all the polymers must react with water and bases to a greater or smaller extent. Since the thermolysis of polymers results in the initial evolution of CO_2, the presence of C atoms linked to two O atoms is desirable. The system of bonds must be conjugated in order to explain the intense colour of the polymers. The reaction of the polymer with ammonia should give rise to amides, whose interaction with water should lead to the appearance of carboxy-groups. A careful study[128] involving ultraviolet and infrared spectroscopy and chemical and X-ray diffraction analyses made it possible to attribute to the polymer structure (IX), which satisfies all these requirements:

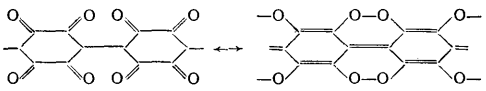


(IX) (X)

A further attractive feature of this structure is that it presupposes the existence also of an ionic pyrylium-like resonance form (X), which is highly stable and deeply coloured. Structure (IX) can be completed in different ways, but 1,2- or 2,3-addition of a C_3O_2 molecule to the ends of the macromolecule appears most likely; five-membered rings with ketenyl groups than arise.

Incidentally, an analogous structure had been proposed somewhat earlier by Ziegler on the basis of purely chemical considerations[137,167], but his work was apparently unknown to Smith et al.[128] Subsequent investigations[127,132,133,168] were consistent with structure (IX).

However, we believe that structure (IX) is not the only one possible. The resonance structures (XI)–(XII) which we put forward are entirely consistent not only with the requirements specified by Smith et al.[128] but also with infrared spectroscopic data, according to which the bands in the range 920–830 cm^{-1}, which were not identified in other studies, can be assigned to the peroxide group C–O–O–C:[169]



(XI) (XII)

In almost all the investigations which have been carried out the low stability of the polymers $(C_3O_2)_x$ was emphasised. We may note that this is true only of polymers obtained at comparatively low (less than 373 K) temperatures. Such polymers are extremly hygroscopic, water vapour altering their structure with evolution of CO_2 and the appearance in the infrared spectrum of bands due to the OH, COOH, ≡CH, and CH_2 groups; the products of the polymerisation of a moist monomer have the same spectrum[169]. The low-temperature polymers are readily soluble in water, giving red solutions. The amount of the soluble fractions diminishes with increase of the polymerisation temperature and the product obtained at 673 K is almost insoluble not only in water but also in dilute alkalies[128]. The available information about the solubility in organic solvents is contradictory. Thus polymerisation at 293 K in hexane gives rise to products which are readily soluble in ethanol but sparingly soluble in hexane; a polymer sparingly soluble in ethanol and chloroform and insoluble in hexane is formed at the same temperature in the gas phase[166]. The polymer obtained in ether[137] is readily soluble in acetone and methanol and sparingly soluble in dioxan and phenols. It has been claimed[128] that these polymers are altogether insoluble in ethanol, acetone, chloroform, carbon tetrachloride, benzene, and xylene. Effective solvents for the low-molecular-weight fractions are dimethyl sulphoxide and dimethylformamide[132,133]. At any rate it is clear that the solubility is determined mainly by the degree of polymerisation; it has been found that the polymer obtained at 373 K contains 5–10 [168] or 5–6 [133] C_3O_2 units.

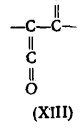
The heat of formation of $(C_3O_2)_x$ from the gaseous monomer is ~137 kJ mol^{-1}.[170] The available information about the thermal stability of polymers is also contradictory. According to Diels and Wolf[117] and Porejko et al.[135], the decomposition begins at a temperature as low as 310 K and CO_2 is evolved. Klemenc and coworkers[126,127] shift the temperature limit to ~373 K. However, careful studies[128,168,171] have demonstrated the high stability of the polymers. At 373 K the polymerisation of C_3O_2 is accompanied by the evolution of small amounts (~1%) of CO_2 and CO, which rise to 2.5 and 6% respectively at 473 and 573 K, but these gases are not the products of the thermal decomposition of the monomer or polymer. The polymer itself begins to decompose only above 573 K, whereupon its colour deepens and its oxygen content falls, but even at the temperature of red heat the polymer

nevertheless still contains a certain amount of oxygen (cf. Ciusa[89]). With increase of temperature, there is an increase of the intensity of the diffraction bands; the X-ray spectrum at 1773 K resembles that of carbon black with the particles sizes L_a = 4.5 nm and L_c = 1.4 nm [168] (cf. also Schmidt et al.[138]). The polymers obtained at 373–393 K have an extremely high surface area (~20 $m^2\ g^{-1}$) and their particle size is ~100 nm according to electron microscope data[171].

According to Mrozowski and Wobshall[130] and Schmidt et al.[139], the non-heat-heated polymer does not give rise to an EPR signal. Quite different information is contained in reports of studies[132,133,172] where the EPR spectra of the $(C_3O_2)_x$ block polymers were investigated in detail. The spectra of the polymers $(C_3O_2)_x$ obtained at 303, 333, and 363 K show an intense slightly asymmetric line, whose intensity corresponds to a spin concentration of 2.5×10^{18} spins g^{-1}; the spectrum of $(C_3O_2)_x$ obtained at 378 K shows also a second line, corresponding to a spin concentration of 2×10^{19} spins g^{-1}, the relative intensities of these two lines being different in the spectra of different specimens. The paramagnetism of the polymers obeys the Curie–Weiss law. The results of the analysis of the line form, the saturation phenomenon, the *g*-factor, and the hyperfine structure of the EPR signals suggested that the paramagnetism of $(C_3O_2)_x$ is due to electronic transitions between individual conjugation regions; the spin concentration ~2.5×10^{18} spins g^{-1} corresponds to a single spin per 600 macromolecules if one assumes that the degree of polymerisation is 6. Since contact with moisture alters the colour of the polymer, causes a gradual decrease of the intensity of the ketenyl signals in the infrared spectra, and leads to a rapid disappearance of the EPR signal, presumably the keto- and keteno-groups are responsible for the generation of relatively stable paramagnetic centres. The possible structures of the resonance forms of the radical-ions have also been published[133]. Irradiation of $(C_3O_2)_x$ with visible light leads to an additional generation of paramagnetic centres; this photoprocess is reversible[132]. The fluorescence of the soluble component of $(C_3O_2)_x$ has also been investigated.

The electrical conductivities of the polymers obtained from the monomer in ethereal solution at 293 K have been studied[140]. The observed conductivities were in the range 10^{-7}–10^{-9} $\Omega^{-1}\ cm^{-1}$ and were poorly reproducible owing to the high hygroscopicity of the polymers. The observed activation energy is close to 1.8 eV. Taking into account the method of synthesis, these results can be attributed only to low-molecular-weight oligomers $(C_3O_2)_x$, which are amorphous according to X-ray diffraction measurements[140].

There may exist also another form of $(C_3O_2)_x$, obtained when the monomer is polymerised in a polar solvent such as nitromethane[136,141]. The study of the chemical properties and infrared spectra of the polymerisation products made it possible to attribute to them the structure of a polyketone (XIII) with a degree of polymerisation of 3–4:



(XIII)

A similar product is obtained in benzene[136] in the presence of catalytic amounts of H_2SO_4 or H_3PO_4. The polymerisation mechanism is neither ionic nor radical and it has been suggested[136] that the reaction proceeds via the intermediate formation of a lactone. The density of polymer (XIII) is lower than that of the usual polymer obtained in ethereal solution (1.22 and 1.61 g cm^{-3} respectively). Polymer (XIII) consists of a very hygroscopic brown powder, which is readily soluble in dimethylformamide and alkalies. However, the dark-brown colour is characteristic also of the radiation polymers $(C_3O_2)_x$, about the structure of which there is no doubt. Since structure (XIII) does not contain a system of conjugated bonds, the deep colour is so far unexplained and the results of Porejko and Gabara[141] must be treated critically.

V. CARBON SUBSULPHIDE POLYMERS

Carbon subsulphide C_3S_2, obtained for the first time by Lengyel[173] by exposing carbon disulphide CS_2 vapour to an electric arc, is a structural analogue of the suboxide C_3O_2 and exhibits an even greater tendency to polymerise. Although C_3S_2 can be obtained also by heating CS_2 vapour to 1273–1373 K in a quartz tube[174], different modifications of Lengyel's method are still being used[175,176], but any method of synthesis involves the formation of large amounts of the polymer $(C_3S_2)_x$.

At room temperature liquid C_3S_2 polymerises spontaneously in several days and at 373 K in several minutes, while on rapid increase of temperature C_3S_2 is converted into $(C_3S_2)_x$ explosively. Solutions of C_3S_2 in CS_2 at concentrations up to 1% are stable on storage in the dark but at higher concentrations slow polymerisation takes place. This also occurs in dilute solutions in sunlight[174]. Acids and alkalies have a catalytic effect[176]. At pressures ranging from 150 to 240 MPa C_3S_2 is exothermically converted into a product fully analogous to a thermopolymer, while the polymer $(CS_2)_x$ obtained from CS_2 at a pressure of 270–450 MPa and a temperature in the range 438–553 K is slowly converted into $(C_3S_2)_x$ under the usual conditions[175]. Illumination of CS_2 with ultraviolet light (253.7 nm) also yields the polymer $(C_3S_2)_x$ together with other products[177].

It has been established[174] that the rate of polymerisation depends little on the C_3S_2 concentration and is proportional to the surface area of the vessel. The order of the reaction is close to second, but in the presence of a large surface area of the reaction vessel deviations from the second order towards the first occur. One of the possible explanations is that at the beginning two C_3S_2 molecules react with one another in the gas phase and the interaction product then polymerises on the walls of the vessel[174].

The polymer $(C_3S_2)_x$ is a black graphite-like substance insoluble in all usual solvents. The product obtained at low temperatures (below 373 K) is soluble in boiling concentrated NaOH solution, being precipitated on acidification. The infrared spectroscopic data for the polymer[175,178–181] differ somewhat from one another (in some instances[180,181] this was explained by the presence of traces of moisture during polymerisation), but the results show that the $(C_3S_2)_x$ structure is fully analogous to that of $(C_3O_2)_x$; the X-ray diffraction patterns of these polymers are also similar. On heating, the decomposition of $(C_3S_2)_x$ begins near 673 K and is accompanied by the evolution of C_3S_2 and traces of CS_2, while the residue contains carbon and sulphur[180]. According to other data[175], the monomer is not evolved on vacuum pyrolysis, only the elimination of CS_2 being observed, and the residue is a dark-red carbon like product which still contains much sulphur [~39% compared with 64% in $(C_3S_2)_x$].

The EPR spectra of $(C_3S_2)_x$ obtained at 448 K give a spin concentration of 2.5×10^{20} spins g^{-1}. Heat treatment of the polymer *in vacuo* or in an atmosphere of helium at temperatures up to 973 K has little effect on the intensity of the EPR signal, while in the presence of air it leads to an increase of signal intensity up to a temperature of ~873 K.[130] The order of magnitude of the electrical conductivity of

$(C_3S_2)_x$ is ~10^{-6} Ω^{-1} cm^{-1}.[175] It is not without interest that the reaction of sulphur with anthracene at 673 K [182] yielded a polymer containing 54% of sulphur and insignificant amounts of H and O, which is also fairly close to the elemental composition of $(C_3O_2)_x$ (see also Wibaut and Kam[92]). The electrical conductivity of this product proved to be only 3×10^{-3} Ω^{-1} cm^{-1}; no data concerning the structure are available.

VI. CONCLUSION

The polymers discussed in this review, which have a system of conjugated bonds, should be in the main semiconductors. However, their properties, particularly their electrophysical properties, have so far been inadequately investigated. Their further study and the preparation on their basis of new materials with interesting properties are worthwhile. For a specific search for such materials, it is extremely important to know the properties of the initial polymers. However, it is clear that the properties described above most probably refer only to individual specimens. For example, one cannot estimate the accuracy of the electrical conductivity measurements; it is undoubtedly low owing to the inhomogeneity of the materials and surface effects. Unfortunately there are no reliable methods for determining the degree of polymerisation of insouble polymers. Reliable characteristics could be obtained for single-crystal specimens. However, there are fundamental difficulties associated with the fact that, when coplanar blocks attain a length of 35–40 units, the coplanar inclusion of subsequent units in the chain becomes energetically less favourable than the formation of a new block unconnected to the previous ones[83]. Depending on the conditions of synthesis, the distribution of blocks with respect to the effectiveness of conjugation may change significantly.

The band structure of the polymers considered is characterised by the fact that the upper valence band and the lower conductivity band are of the π-character. Their theoretical study can therefore be based on models involving the π-electron approximation. In the simplest of the models (the Hückel model) the nature of the π-bands of $(CN)_x$ in modification (II) has been discussed[183]. It has been shown that in such systems the alternation of bond lengths and hence of resonance integrals is insignificant. It is more important that the difference between the electronegativities of the C and N atoms, described by the difference between their Coulombic integrals, makes the main contribution to the energy gap of the polymer with a fully filled π-band. The electronic structure of $(CN)_x$ in modifications (II) and (IV) has also been calculated within the framework of the extended Hückel method using crystal orbitals[184]. The application of this model to modification (II) resulted in the overlap of the lower vacant π-band (conductivity band) and the upper occupied σ-band (valence band), formed by the lone electron pairs of nitrogen, which give rise to a ground state of the metallic type.

In discussing these results one should not, incidentally, neglect the fundamental defects of the method, which have been pointed out, for example, by Dewar[185] and which are particularly pronounced for heteroatomic systems of the type under consideration. It may be that the result obtained is an artefact of the Hückel model. The fact that $(CN)_x$ with structure (IV) exhibits in the same calculations a considerable stability and an energy gap of ~1.4 eV of the semiconductor type is in better agreement with experimental results. The calculation[184] on the parquet polymer $(C_3N)_x$ also led to a metallic conductivity, since, as a consequence of the odd number of π-electrons in the unit cell, the upper valence π-band is partly filled. Clearly, paracyanogen (III) should exhibit, within the framework of this model, a metallic character like graphite, which is fully consistent with experimental data[76].

According to modern ideas concerning the electronic structure of polyconjugated polymers[186], the ordered system made up of the graphite network by the replacement of certain carbon atoms by boron or nitrogen atoms should be ferromagnetic, since its total spin in the ground state is infinite. Difficulties associated with the creation of polymeric ferromagnetic materials of this kind have recently been noted by Buchachenko[187].

The band structure of the remaining polymers deals with in the review has not apparently been studied. It is clear from general considerations that the difference between the Coulombic integrals for the C, O, and S atoms should lead to the absence of overlap of the valence and filled bands and hence to semiconducting properties of the polymers, and the energy gap in the case of $(C_3S_2)_x$ should be smaller than in the case of $(C_3O_2)_x$.

It is appropriate to point out a number of considerations concerning specific ways of increasing the electrical conductivity of the polymers considered. Among purely physical methods, one may indicate the application of a high pressure[188], which, by reducing the internuclear distances and by increasing the overlap of the atomic orbitals, leads to the overlap of a number of bands, as a consequence of which a typically semiconducting system becomes metallic. A remarkable example of this kind is provided by elemental sulphur[189]. In principle, there is then a possibility of transitions to a structure with another crystal lattice. However, chemical methods are more effective and easier to apply, for example the intercalation already mentioned. The scope of this method is extremely wide, which can be illustrated by the following example. When partly oriented films of polyacetylene $(CH)_x$ are doped with donors of acceptors (Na, I_2, AsF_5, etc.), the conductivity increases from 10^{-10}–10^2 Ω^{-1} cm^{-1}, i.e. by twelve orders of magnitude, and materials of *p*- and *n*-types are obtained[190]. The results of the intercalation of hexagonal boron nitride $(BN)_x$, which is converted from a typical insulator to a conductor following the introduction of $S_2N_6F_2$, are even more striking[191].

Certain conjugated polymers have already found applications as the working materials of thermoresistors and tensotransducers, many parameters of which are superior to those of the usual industrial specimens[81]. A high-quality *p*–*n* junction with very effective rectifying properties has been prepared[192] from $(CH)_x$ films of different types. Thus one may expect interesting electrophysical properties of intercalated polymers, to the discussion of which this review has been devoted, and in the future new materials important for modern technology may be obtained. Advances in this field can depend to a large extent on the preparation of single-crystal specimens of the corresponding polymers.

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