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Semiconducting Pyropolymers

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Model structures which explain the electrical and the paramagnetic properties of semiconducting pyropolymers are proposed. The development of paramagnetic clusters during the formation of these polymers is demonstrated, and the generality and the thermodynamic efficiency of this process are stressed. The problems encountered when applying the theory of electrical conduction in heterogeneous materials and the theory of flows to semiconducting pyropolymers are discussed. Transport phenomena involving the charge carriers in these polymers are analysed by the theory of electronic states in disordered systems. The temperature dependence of the electrical conductivity is shown to obey Mott's law over a wide range of temperature. Quantitative relationships for the pressure dependence of the electrical parameters of powdered semiconducting pyropolymers are obtained, and the influence of the structure of these materials on their electrical and paramagnetic properties is examined. 103 references.

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I. INTRODUCTION

Many polymers showing semiconducting properties have been synthesised and investigated[1-14]. Their electrical[1-7], photoelectric[1-4,10,13,14], catalytic[1-3,15,16], and paramagnetic properties[1-3,7,16-22] have been highlighted, and the materials have been used in optical information storage systems[13,14]. The practical realisation of superconductivity with a high critical temperature by using polyconjugated polymers has been predicted[23], and though the prediction has not yet been proved correct it has made a very important contribution to the development of the physics and chemistry of molecules with conjugated bonds[16], whose photochemical and radiation-chemical stability is discussed in detail in Ref. 24.

Comprehensive theoretical studies[16,18-31] of the electronic structure and of the paramagnetism of polymers with conjugated bonds have been carried out, the properties of their molecules have been broadly characterised, and experimental observations of their optical spectra have been explained. In this context the work of Ovchinnikov[30,31] deserves special mention for combining a physical demonstration with a theoretical proof of the development of ferromagnetism in alternant organic systems. In spite of these achievements, however, a general theory of the physical properties of polymeric semiconductors is still awaited. The need for a special theory has even been questioned: as an alternative, the properties of these polymers could be described in terms of the theory of disordered systems[32-42].

In this review we shall examine from the standpoint of the theory of the electrical properties of disordered systems the relationship between the electrical conductivity (or the paramagnetism) and the structure of semiconducting pyropolymers, prepared mainly from polyacrylonitrile (PAN). The choice of these materials was dictated by the abundance of the data on the thermal transformations of PAN,[1,8,12,43-51] and by the recent publication of monographs dealing with the semiconducting properties of the PAN pyropolymers[1,2,7].

No attempt will be made to include the whole of the information on the thermal reactions of PAN and on the properties of the semiconducting products of these reactions. Published work will be mentioned only if it contains data on the structural, electrophysical, or paramagnetic properties of these materials, or if it can help to build a concrete model of the structure of semiconducting pyropolymers.

II. STRUCTURAL FEATURES AND ELECTRICAL CONDUCTIVITY OF PYROPOLYMERS

Semiconducting pyropolymers can be treated as microheterogeneous systems consisting of electrically conducting polyconjugation regions separated by barrier layers[1-3,7]. The volume fraction of the polyconjugation regions is determined by the technological conditions used in the preparation of the pyropolymer: it increases monotonically with the temperature of heat treatment, and thus it affects very markedly the interactions between these regions[52,53]. For this reason semiconducting pyropolymers prepared under different conditions cannot be described by the same type of heterogeneous model.

In order to produce a concrete model of the structure of the heterogeneous system we must first of all determine the volume fractions, the size, the types of interaction, and the distribution of the components. So far this information is available only for semiconducting pyropolymers based on PAN.[52-55]

1. Determination of the Concentration of the Polyconjugation Regions and of the Structural Parameters of Semiconducting Pyropolymers

The concentration of the components of heterogeneous semiconducting pyropolymer systems is determined by monitoring the change in an extensive factor with heat treatment temperature (T_{form}). The most convenient and easily measured extensive factor in these systems is the density, which increases with the T_{form} value of the semiconductor[53]. This suggests that the polyconjugation regions are relatively dense, and the interlayers between these regions relatively loose.

The density γ of a heterogeneous system is defined by the expression

$$\gamma = \sum_i V_i \gamma_i , \qquad (1)$$

where V_i is the volume fraction and γ_i is the density of the i-th phase. In the case of two-component systems, to which semiconducting pyropolymers can be assigned to a first

approximation, Eqn.(1) takes the form

$$\gamma = V_1\gamma_1 + (1-V_1)\gamma_2 , \qquad (2)$$

where γ_1 and γ_2 are the densities of the conducting and the non-conducting component respectively, and V_1 is the volume fraction of the polyconjugation regions. Obviously, $V_2 = 1 - V_1$ is the volume fraction of the non-conducting component. Solving Eqn.(2) for V_1 we obtain

$$V_1 = \frac{\gamma - \gamma_2}{\gamma_1 - \gamma_2} . \qquad (3)$$

In the case of PAN semiconductors the volume fraction V_1 has been determined[52,53] by formula (3) by arbitrarily identifying γ_1 with the density of the sample obtained at 1100° (assumed to consist almost exclusively of fully developed polyconjugation regions), and γ_2 with the density of the sample obtained at 200° (in which the amount of polyconjugation is negligible). This involves the assumption that the densities of the conducting and of the non-conducting component are independent of the heat-treatment temperature (T_{form}) of the sample, i.e. that only the relative amounts of the two components are affected by the pyrolysis temperature. This hypothesis is supported by studies of the frequency dependence of electrical conductivity[56] and of the frequency spectrum of the current noise[57] in pyrolysed PAN: the results confirm that the basic structure of the polyconjugation regions is unchanged by an increase in the pyrolysis temperature of the initial polymer. Though an analysis of the formation of semiconducting pyropolymers suggests[44-51] that both γ_1 and γ_2 should increase slightly with pyrolysis temperature, the inequality $\gamma_1 > \gamma > \gamma_2$ must always be satisfied, and therefore the volume fractions calculated by formula (3) cannot be greatly in error.

Table 1. Effect of the formation temperature T_{form} of PAN on the concentration of PMC, on the distance d between them, on the volume fraction V_1, the average volume $\bar{v}$, and the average linear size L of the polyconjugation regions, and on the average distance S between the "surfaces" of these regions (measurements in air)[53].

T_{form}, °C	$10^{-19}N$, spins cm^{-3}	V_1	$\bar{v}$ (Å)³	L, Å	S, Å	d, Å
300	$9.5\cdot10^{-2}$	0.07	$7.7\cdot10^{4}$	42.5	60.8	103.3
350	$3.3\cdot10^{-1}$	0.16	$5.0\cdot10^{4}$	36.9	30.7	67.5
400	1.1	0.24	$2.3\cdot10^{4}$	28.4	17.0	45.4
450	2.6	0.30	$1.2\cdot10^{4}$	22.8	11.1	33.9
500	6.7	0.38	$5.7\cdot10^{3}$	17.9	6.7	24.6
550	1.1·10	0.44	$4.0\cdot10^{3}$	15.9	4.9	20.8
600	1.5·10	0.51	$3.4\cdot10^{3}$	14.9	3.8*	18.7
650	1.7·10	0.58	$3.3\cdot10^{3}$	15.0	3.0*	18.0
700	1.3·10	0.62	$5.4\cdot10^{3}$	17.5	2.9*	20.4
750	5.1	0.72	$1.4\cdot10^{4}$	24.2	—	27.0
800	1.4·10	0.81	$5.8\cdot10^{5}$	83.4	—	89.3
850	$5.2\cdot10^{-2}$	0.85	$1.6\cdot10^{6}$	117.7	—	124.4
900	$2.1\cdot10^{-2}$	0.88	$4.1\cdot10^{6}$	161.5	—	168.3
1000	$1.5\cdot10^{-2}$	0.95	$6.3\cdot10^{6}$	185.7	—	188.7

*These values have no real physical significance.

Table 1 (taken from Ref.53) shows the volume fractions of polyconjugation regions in PAN pyropolymers, calculated by formula (3) as a function of the thermolysis temperature. The Table also shows the average effective volume corresponding to one paramagnetic centre (PMC)

$$\bar{v} = V_1/N , \qquad (4)$$

where N is the number of PMC in 1 cm^3, and the average linear size

$$L = (V_1/N)^{1/3} \qquad (5)$$

of the polyconjugation regions. On the assumption that the unpaired electrons are uniformly distributed throughout the sample, and localised on specific atoms or within their coordination sphere, we can use the expression

$$d = N^{-1/3} \qquad (6)$$

for the average distance between PMC. On the additional assumption that the distribution of polyconjugation regions over the sample is uniform and random, and using Eqns.(4) to (6), we can define an average effective distance S between the "surfaces" of the polyconjugation regions as

$$S = \frac{1 - V_1^{1/3}}{N^{1/3}} \quad \text{or} \quad S = d - L . \qquad (7)$$

Since the parameter N is affected by atmospheric oxygen, all the quantities calculated by Eqns.(4)–(7) (i.e. $\bar{v}$, L, d, and S) also depend on the conditions under which N was determined. We should note that V_1 and N (and therefore also $\bar{v}$, L, d, and S) are parameters of the structure of the semiconducting pyropolymers: the change in these parameters during the formation of the polymer reflects the growth of the polyconjugation regions in relation to the external factors. This is illustrated by the data in Table 1, from which it is clear that as the heat treatment temperature of the PAN is increased the volume fraction of the polyconjugated regions also increases to a value in excess of 50% at temperatures above 600°, and the distance between polyconjugation regions becomes shorter.

The variation of L with the thermolysis temperature of the sample yields valuable information on the growth of the polyconjugation regions during the formation of the semiconducting pyropolymers. At first sight the decrease of L with increase in heat treatment temperature (to 600°) appears inconsistent with studies of the absorption[43] and fluorescence[51] spectra of PAN at various stages of heat treatment. According to those studies more intensive thermolysis causes cross-linking of the continuous conjugation regions, reflected by a shift in the fluorescence spectrum in the near i.r. and by an increased absorption in the long-wavelength tail of the spectrum, i.e. by an increase in the length of the polyconjugation blocks. However, this apparent contradiction is easily dismissed if we consider the mechanism of thermolysis of PAN [46,51] to give polyconjugated systems with a wide distribution in size of the polyconjugation blocks[8]. Obviously, the rate of formation of these blocks (after an initial stage in the formation of the semiconducting pyropolymers) increases with the formation temperature T_{form} more rapidly than their rate of growth and coalescence, causing N to increase and L to decrease. At this stage in the heat treatment the pyropolymer is enriched in polyconjugation regions mainly through an increase in their number. On the other hand, at temperatures $T_{form} > 600°$ the polyconjugation regions can also grow and coalesce, and the number of PMC decreases (see Table 1).

Information on the electronic states of semiconducting pyropolymers and on the distribution and interaction of their components over microscopic volumes can be obtained from the ESR spectra. The ESR lines of PAN semiconductors with formation temperatures $T_{form} \leqslant 300°$, $300° < T_{form} < 600°$, and $T_{form} \geqslant 600°$ have a Gaussian, a mixed, and a Lorentzian form respectively[55]. The line width and the spin–lattice relaxation time T_1 decrease as T_{form} increases[58]. By studying samples containing different numbers of PMC a strong concentration dependence of the rate of spin–lattice relaxation was observed[58] (see Table 2), as in polyphenylacetylene

samples thermolysed at different temperatures[59,60]. This indicates exchange interaction between the PMC in thermolysed PAN for $T_{form} > 300°$, increasing with the thermolysis temperature of the polymer. We know[61] that the intensity of the exchange interaction is very sensitive to the distance between the PMC, the effect being strong at distances <10 Å. Thus we may conclude that the distance between some of the PMC in PAN pyropolymers with $T_{form} > 300°$ is less than 10 Å.

Table 2. Effect of the formation temperature T_{form} of PAN on the concentration N of PMC, on the width ΔH of the ESR line, on the average distance d between PMC, on the average number K of PMC in each cluster, and on the time T_1 (measurements in vacuum).[58]

T_{form}, °C	$10^{-19}N$, spins cm^{-3}	ΔH, Oe	d, Å	K	T_1, s
300	$9.7\cdot10^{-1}$	16	46.9	2.2	$1.1\cdot10^{-2}$
400	6.0	15	26.5	36	$3.4\cdot10^{-3}$
500	$2.0\cdot10$	4.1	17.1	238	$2.1\cdot10^{-4}$
600	$2.9\cdot10$	1.8	15.1	753	$3.9\cdot10^{-5}$

If the true distance between the PMC is calculated by formula (6) it becomes impossible to account for the observed exchange interaction, since at the maximum PMC concentration this formula gives $d \geq 18$ Å (Table 1). We must assume that in the samples prepared at $T_{form} > 300°$ the unpaired electrons are delocalised within the separate polyconjugation regions, i.e. they are π-electrons. Under these conditions the distance between the unpaired electrons of neighbouring polyconjugation regions (at the moment of nearest approach) is the quantity S, given by formula (7). But even in this case the presence of exchange interaction between the PMC in samples containing less than 5×10^{19} spins cm^{-3} cannot be accounted for. To resolve these inconsistencies we must postulate the formation of clusters (swarms) within which the distance between PMC is <10 Å in PAN pyropolymers formed at $T_{form} > 300°$: under these conditions the exchange integral becomes large. The formation of paramagnetic clusters during the preparation of semiconducting pyropolymers is a direct consequence of the local activation effect[62], which causes PMC to be formed preferentially near other PMC. The same effect has been used[63] to explain the deviation from a uniformly random distribution of the PMC in poly(vinyl chloride) samples with a modified surface.

The average number of PMC in separate paramagnetic clusters can be estimated by the method developed by Vannikov and coworkers[2,7] to determine the average number of polyconjugation regions per unit length from the current–voltage characteristic (CVC) of the sample. The method is based on the theory[64] of the CVC of heterogeneous systems consisting of layers with good and with poor electrical conductivity connected in series, the poorly conducting layers acting as barriers to the charge carriers. Ignoring the resistance of the polyconjugation regions, we can express the density j of the current flowing through the barriers as a function of the applied potential by the Petritz formula[2]

$$j = Mep\left[\exp\left(-\frac{\varphi}{k_BT}\right)\right]\left[\exp\left(\frac{e\Delta V}{k_BT}\right) - 1\right], \quad (8)$$

where p is the average concentration of the majority carriers in the polyconjugation regions, ϕ is the height of the potential barrier, ΔV is the potential step at each barrier, k_B is Boltzmann's constant, T is the absolute temperature, M is a parameter independent of ϕ and of the same order as the thermal velocity of the current carriers, and e is the electronic charge. In the low-field region we have $\Delta V \ll k_BT/e$, and Eqn.(8) becomes[2]

$$j = \frac{Mpe^2\Delta V}{k_BT}\exp\left(-\frac{\varphi}{k_BT}\right).$$

Let n_1 be the number of polyconjugation regions per unit length connected in series. The potential step ΔV then becomes[2]

$$\Delta V = V/n_1 l = E/n_1, \quad (9)$$

where V is the voltage applied to the sample, E is the field strength, and l is the thickness of the sample. In the strong field region we have $e\Delta V \gg k_BT$, and by combining (8) and (9) we obtain[2]

$$j = Mep\exp\left(-\frac{\Delta E}{k_BT}\right), \quad (10)$$

where $\Delta E = \phi - BV$, and $B = e/n_1 l$. Thus the parameter B can be obtained from the current–voltage characteristic, and used to calculate n_1.

The exchange interaction arises because of the overlap of the π-electron clouds in the polyconjugation regions responsible for the PMC clusters. In the presence of strong exchange interaction the individual PMC clusters behave as single spin-systems: within each paramagnetic cluster the barriers are practically transparent to the charge carriers, and the reistance of the cluster can be neglected in comparison to that of the layers which separate the clusters. Therefore the CBC can be used to determine effectively the number of PMC clusters per unit length. The ratio

$$k = N/n_1^3 \quad (11)$$

defines the average number of polyconjugation regions forming separate clusters, i.e. the structural parameter responsible for the mechanism of electrical conduction and of paramagnetic relaxation in these materials.

As Table 2 shows, the size of the paramagnetic clusters (characterised by the parameter k) increases with T_{form}; at the same time the spin–lattice relaxation time T_1 decreases. These results suggest that (as in the case of thermolysed polyphenylacetylene[59]) the paramagnetic relaxation occurs through the clusters. The increase in k with T_{form} also shows that in PAN semiconductors with $T_{form} < 350°$ exchange interaction occurs through nearest-neighbour PMC, whereas in samples with $T_{form} > 350°$ the interaction also involves PMC at distances much greater than the radius of the coordination sphere. This conclusion is confirmed by the gradual disappearance of the saturation effect on the ESR line as T_{form} is increased, the PAN semiconductor becoming non-saturable for $T_{form} > 600°$.[58] This observation shows that when $T_{form} > 600°$ exchange interaction between the paramagnetic clusters sets in.

The organisation of PMC into clusters during the formation of semiconducting pyropolymers enhances the degree of delocalisation of the π-electrons, and this should lead to a decrease in the internal energy of the system: in other words, cluster formation is a thermodynamically favourable process. Cluster formation of the PMC is, essentially, the first step in the formation of graphitisation nuclei, and can be treated as a self-organisation process: the formation of ordered structures in disordered systems. A recent monograph[65] is devoted to self-organisation processes in a wide variety of systems.

Thus, the above results lead to the conclusion that semiconducting pyropolymers can be treated (with adequate precision) as micro-heterogeneous, two-component, electronically

non-uniform systems consisting of regions with high and with low electrical conductivity. We can therefore attempt to apply the theory of heterogeneous materials to a description of the electrical conductivity of these polymers.

2. Theory of the Electrical Conductivity of Disordered Systems and Electrical Conductivity of Semiconducting Pyropolymers

The effective medium method has been used[66,67] in a theoretical calculation of the electrical conductivity σ of two-component (composite) systems in which one of the phases forms a matrix at all finite concentrations, and also of random mixtures in which the particles are fully disordered and do not form any regulating structure. Formulae (12) and (13) were obtained[66,67] for the matrix systems and for the random systems respectively:

$$\sigma(V_1) = \sigma_2\left[1 + \frac{V_1}{(1-V_1)/3 + \sigma_2/(\sigma_1-\sigma_2)}\right] \qquad (12)$$

$$\sigma(V_1) = \frac{(3V_1-1)\sigma_1 + (3V_2-1)\sigma_2}{4} + \left[\frac{[(3V_1-1)\sigma_1 + (3V_2-1)\sigma_2]^2}{16} + \frac{\sigma_1\sigma_2}{2}\right]^{1/2}, \qquad (13)$$

where σ_1, σ_2, V_1, and V_2 are the electrical conductivities and the volume fractions, respectively, of the conducting and of the non-conducting component of the heterogeneous system.

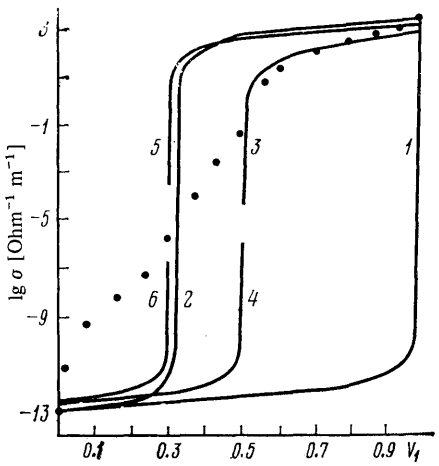


Figure 1. Electrical conductivity against volume fraction of polyconjugation regions in PAN semiconducting pyropolymers. The points are experimental, the full lines are calculated by: *1*) Eqn.(12), *2*) Eqn.(13), *3*) Eqn.(15) with $V_1 = 0.5$, *4*) Eqn.(17) with $V_c = 0.5$, *5*) Eqn.(15) with $V_c = 0.3$, *6*) Eqn.(17) with $V_c = 0.3$.

Some corrections are needed before Eqns.(12) and (13) can be used to describe the concentration dependence of the conductivity of micro-heterogeneous semiconducting pyropolymers, because these equations were derived for systems of chemically non-interacting macroscopic regions (densely compressed mixtures of particles) of high and of low conductivity. However, information on the structural details of the heterogeneous materials can be obtained from the deviation of the experimental $\sigma(V_1)$ dependence from the dependence calculated by Eqns.(12) and (13). This is illustrated in Fig.1 by curves plotted from the data of Table 1.

We note the substantial difference between the experimental $\sigma(V_1)$ plot and that calculated by formula (12) for semiconducting PAN pyropolymers. Hence, the structural model of a two-component matrix system with equally spaced inclusions of equal size, for which Eqn.(12) was derived, is not applicable to semiconducting pyropolymers. The $\sigma(V_1)$ dependence calculated by formula (13), however, is close to the experimental curve for $V_1 \geq 0.5$.

As Fig.1 shows, formula (13) predicts a critical concentration ($V_c \approx 0.333$) of the electrically conducting component at which the conductivity of the two-component system begins to rise steeply. This means that in a system with $V_1 > V_c$ we expect clusters of particles of the conducting component to permeate the whole system. Thus, Odelevskii's generalised conductivity theory[67] for random two-component mixtures implies the important concept of a critical (threshold) concentration V_c:

$$\sigma(V_c) = \frac{\sigma_2 + \sqrt{\sigma_2^2 + 8\sigma_1\sigma_2}}{4}. \qquad (14)$$

A strict mathematical definition of the threshold concentration (flow threshold), given in Ref. 68, laid the foundations of the theory of flows. A detailed analysis of the basis of this theory and of its application to the calculation of the electrical parameters of highly inhomogeneous media can be found in earlier reviews[35,36]. The flow thresholds calculated for the covalent bond problem (diamond type lattice) and for the lattice site problem (simple cubic lattice) are close to the values given by formula (13) (see Table 5.1 of Ref.36).

The following dependences have been obtained[37,38,40] by the theory of flows: for $V_1 \geq V_c$

$$\sigma(V_1) = \sigma_1(V_1 - V_c)^t \qquad (15)$$

$$\sigma(V_c) = \sigma_1(\sigma_2/\sigma_1)^s = \sigma_1 h^s; \qquad (16)$$

and for $V_1 < V_c$

$$\sigma(V_1) = \sigma_2(V_c - V_1)^{-q} = \sigma_1 h(V_c - V_1)^{-q}. \qquad (17)$$

In these expressions t, s, and q (for three-dimensional systems) have the following values[38]: $t = 1.6$, $s \approx 0.62$, and $q = t/s - t$; σ_1, V_1, and V_c are the electrical conductivity, the volume fraction, and the threshold concentration of the metallic component of the two-component system, σ_2 is the electrical conductivity of the dielectric component. If the parameter $h = \sigma_2/\sigma_1$ is very small but finite the dielectric components begin to shunt the conducting cluster when the difference $V_1 - V_c$ is small enough; under these conditions the singularity of the function $\sigma(V_1)$ at $V_1 = V_c$ disappears, and $\sigma(V_1)$ becomes a smooth function increasing monotonically from σ_2 to σ_1.[38] In the immediate vicinity of V_c Eqns. (15) and (17) are not valid, and become indistinguishable[38]. It has been suggested[37,38] that in the transition region the $\sigma(V_1)$ dependence is determined by the parameter $\Delta = h^m$ (where $m = s/t$), called the width of the transition.

Formulae (15) and (17) accurately describe the electrical conductivity of two-component systems consisting of materials with widely different conductivities. Typical examples of these systems are the cermets, and substances which undergo dielectric—metal phase transitions of the first kind at a particular temperature (for example, transition-metal oxides)[38]. The transition can be "smeared out" by inhomogeneities in the material, and extend to relatively low temperatures. As a result, a metallic phase is formed within the dielectric matrix, the volume fraction being determined (between zero and unity) by the heat treatment temperature[69].

An analogous description can be given to the formation of polyconjugation regions (the "metallic phase") in a matrix of the initial polymeric dielectric (such as PAN, poly(vinyl chloride), poly(vinyl acetate), oxidised and cross-linked polyolefins, and some resins) during heat treatment. Indeed, from the standpoint of the structure of the final product the formation of semiconducting pyropolymers and the dielectric–metal transition have a great deal in common. However, when using this analogy the essential difference in nature between these two transitions should be remembered: the phase transition is a physical transformation, but the formation of semiconducting pyropolymers is a chemical transformation. Furthermore, in metals the motion of the delocalised electrons is three-dimensional (though it may be effectively two-dimensional in very thin layers), whereas in the chains of polyconjugation blocks it is one-dimensional[27]. (The existence of one-dimensional metals has been shown[70] to be impossible.) Therefore, the problem of one-dimensional conduction in long conjugated molecular chains is still unresolved[27,39].

As Fig.1 shows, the experimental curve almost coincides with that calculated by formula (15) in the range beginning at $V_1 \cong 0.5$. Hence, for our samples[53] of heat-treated PAN we can assume $V_C \cong 0.5$, which corresponds to $T_{form} \cong 600$ °C. The reality of the high-concentration threshold predicted by the flow theory is consistent with a high level of asymmetry in the configuration of the conducting and the non-conducting regions[40].

The deviation at $V_1 < V_C$ of the experimental $\sigma(V_1)$ plot from the curve calculated by Eqn.(17) is probably due to tunnelling of the electrons through the layers of dielectric material.

We should note that the $\sigma(V_1)$ relationships calculated by Eqns.(13), (15), and (17) and $V_C \cong 0.333$ are practically identical (the width $\Delta = h^m$ of the transition between (15) and (17) is fairly small for semiconducting pyropolymers). This allows us to compare (14) and (16), which leads to the expression

$$h^s = \frac{h + \sqrt{h^2 + 8h}}{4} \quad . \tag{18}$$

The quantity s calculated by Eqn.(18) for h values between 10^{-4} and 10^{-16} lies in the range 0.57–0.51, i.e. it increases very slowly with h.

Thus, the electrical conductivity of semiconducting pyropolymers in which the volume fraction of polyconjugations ("metallic phase") regions is $V_1 > 0.5$ can be described by the theory of flows. From this we may conclude that our proposed method[53] of determining the volume fraction of polyconjugation regions correctly represents the structural features of this type of material.

Useful information on the conduction mechanism has been obtained from the temperature dependence of the conductivity in semiconducting pyropolymers[1–7,71–73]. Most of the experimental results (with a few exceptions) lie on straight-line plots of lg σ against T^{-1}. In some cases these plots include breaks. For example, a study[72] of the temperature dependence of the conductivity of thermolysed PAN samples between 1.7 and 700 K has revealed five linear regions, the activation energy for conduction decreasing with decrease of temperature. This type of change in conductivity with temperature has been discussed[74–76] in terms of the electronic theory of disordered materials[35,36].

We know[35] that the temperature dependence of hopping conduction in the constant activation energy regime is

$$\sigma = \sigma_3 \exp\left(-\frac{\varepsilon_3}{k_B T}\right) \quad . \tag{19}$$

The activation energy (ε_3) for a given temperature is defined by the differential $[d(\ln \sigma)/d(k_B T)]^{-1}$. Hence, using Mott's law

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad , \tag{20}$$

where T_0 and σ_0 are parameters of the chosen model, we find that ε_3 can be expressed as

$$\varepsilon_3 = \frac{1}{4} T_0^{1/4} k_B T^{3/4} \quad , \tag{21}$$

and therefore decreases monotonically (as $T^{3/4}$) when the temperature is lowered.

Mott[41] gives the following expressions for T_0 and σ_0:

$$T_0 = \frac{\beta}{k_B g(\mu) a^3} \quad , \tag{22}$$

$$\sigma_0 = \frac{3 e^2 \nu \Phi_0}{2} \left(\frac{g(\mu) a}{2\pi k_B T}\right)^{1/4} \quad , \tag{23}$$

where a is the radius of the localised states close to the Fermi level, $g(\mu)$ is the density of states at the Fermi level, e is the electronic charge, ν is the phonon frequency, $\Phi_0 \cong 1$ is a constant, and $\beta = 21.2 \pm 1.2$ is a coefficient calculated by the theory of flows[36].

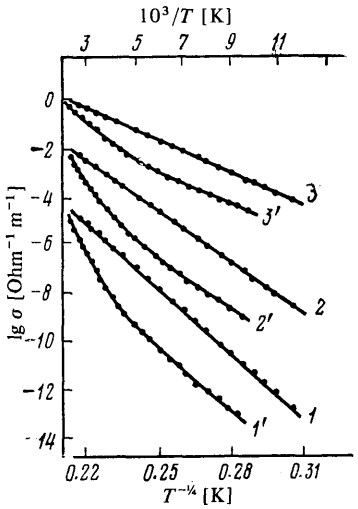


Figure 2. Temperature dependence of the electrical conductivity of PAN semiconducting pyropolymers prepared at different temperatures: *1*) and *1'*) 400°, *2*) and *2'*) 500°, *3*) and *3'*) 600°; *1*), *2*), and *3*) are in lg σ–$T^{-1/4}$ coordinates, *1'*), *2'*), and *3'*) in lg σ–T^{-1} coordinates[74].

The temperature dependence of the electrical conductivity is accurately described by straight lines (Fig.2) between 100 and 450 K when plotted as lg σ against $T^{-1/4}$, confirming that Mott's law (20) is obeyed.

Simultaneous solution of Eqns.(22) and (23) using data from Fig.2 gives unreasonable values of a and of $g(\mu)$ (see Table 3 [74]). Similar results were obtained with polyacene copolymers of the quinone radical type[77]. Therefore $g(\mu)$ was calculated by taking a as one-half of the average distance between polyconjugation regions determined by formula (7). This gave entirely reasonable values of $g(\mu)$ when Eqn.(22) was used, but calculations by Eqn.(23) gave physically

meaningless results (see Table 3). Hence, Eqn.(23) is not applicable to polymeric semiconductors. We note from Fig.2 that the temperature dependence of the conductivity is linear in lg σ against T^{-1} coordinates over relatively narrow temperature ranges, and the ε_3 values for these ranges decrease monotonically as the temperature decreases (see Table 4) [75] in accordance with Eqn.(21).

Table 3. Effect of formation temperature on the parameters of PAN samples[74].

T_{form}, °C	$10^{-4} \cdot T_0$, K	σ_{00}, Ohm^{-1}cm^{-1}	$10^{18} \cdot a^{*}$, cm	$g(\mu)^{*}$, V^{-1} cm^{-3}	$10^{8} \cdot s/2$	$g(\mu)$, eV^{-1} cm^{-3} (calc. by Ref.22)	$g(\mu)$, eV^{-1} cm^{-3}, (calc. by Ref.23)	$10^{-17} \cdot n$	$10^{-6}\mu_0$
400	1.8·10	6.1·10^{12}	1·10^{-5}	1·10^{55}	4.7	1.3·10^{17}	2.2·10^{44}	1.6·10	2.4·10^{5}
500	6.7	5.9·10^{10}	1.7·10^{-3}	5.7·10^{49}	2 4	2.8·10^{18}	7.1·10^{39}	8.2	4.5·10^{3}
600	1.13	3.5·10^{7}	7.1	4.8·10^{38}	1.3	6.5·10^{20}	2.6·10^{33}	3.8	5.7

*Values obtained by solving (22) and (23) simultaneously, using data from Fig.2.

Table 4. Activation energy of PAN semiconductors prepared at 400, 500, and 600° against measurement temperature [the ε_3(exper) values were obained by formula (19), the ε_3(calc) values by formula (21)].[75]

T_{form} = 400° C			T_{form} = 500° C			T_{form} = 600° C		
T, K	ε_3 (exper), eV	ε_3 (calc), eV	T, K	ε_3 (exper) eV	ε_3 (calc), eV	T, K	ε_3(exper), eV	ε_3 (calc), eV
112—124	0.165	0.159	105—113	0.120	0.114	102—108	0.072	0.077
148—162	0.190	0.191	133—147	0.140	0.137	116—126	0.083	0.082
178—194	0.223	0.219	174—190	0.170	0.167	135—151	0.093	0.093
210—232	0.257	0.249	230—264	0.215	0.210	168—188	0.110	0.109
238—280	0.282	0.280	307—425	0.280	0.282	202—232	0.125	0.127
298—431	0.364	0.361	—	—	—	270—374	0.176	0.171

The temperature dependence of the electrical conductivity of semiconducting pyropolymers reflects the structure of these materials. As stated above, pyropolymers can be treated as micro-heterogeneous systems consisting of electrically conducting polyconjugation regions separated by layers of dielectric material. The distance between the polyconjugation regions (and between their clusters) can take a set of values, since their nucleation during pyrolysis is a random process. These inhomogeneous systems can be described by Miller and Abrahams' random resistance network model[35,36], in which the polyconjugation regions are treated as the analogues of donors, and the dielectric layers as analogues of the resistance to the transfer of current carriers between donors. At low temperatures the main contribution to the conduction is that of barrier layers with low values of ε_3. On raising the temperature the contribution from layers with relatively high values of ε_3 becomes significant.

The general definition of electrical conductivity is

$$\sigma = en\mu , \qquad (24)$$

where n and μ are the concentration and the mobility of the current carriers respectively. In the case of semiconducting pyropolymer the parameter n denotes the average number of polyconjugation regions in each cluster, within which the barriers are almost transparent to the current carriers, and therefore $n < N$. Electrical conduction arises mainly from jumps of the current carriers between the polyconjugation regions and between their clusters.

In semiconductors of this type the increase in conductivity with temperature is usually ascribed to an increase in μ;[1-4,7,73] we can therefore write

$$\mu = \mu_0 \exp[-(T_0/T)^{1/4}] \qquad (25)$$

$$\sigma_0 = en\mu_0 , \qquad (26)$$

where μ_0 is a constant, independent of the measurement temperature. The n values, determined by formula (10) from the CVC, are given in Table 3 together with the μ_0 values. We see from Fig.3 that μ increases with the heat treatment temperature. Thus semiconducting pyropolymers are strongly inhomogeneous systems in which electrical conduction is by jumps of variable length over a wide range of temperature. The temperature dependence of the average jump length $\bar{r}$ is given by the expression[36]

$$\bar{r} = \frac{1}{2.73}\, a\,(T_0/T)^{1/4} .$$

The average jump length decreases as T_{form} increases (Fig.4). From Fig.3 and Table 4 we conclude that higher values of mobility correspond to higher values of the activation energy.

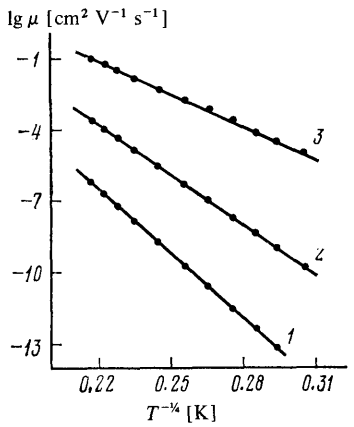


Figure 3. Temperature dependence of the mobility of the charge carriers μ in PAN semiconducting pyropolymers prepared at: *1*) 400°, *2*) 500°, and *3*) 600°.[75]

The current carriers in semiconducting pyropolymers have very low mobilities (Fig.3). Ioffe and Regel'[32-34] tried to explain the low mobilities in amorphous and in liquid semiconductors of various types, but they met some fundamental difficulties, which we shall examine below.

The mobility μ and the coresponding mean free path l of the current carriers with an effective mass m^* at room temperature are interrelated by the expression[33,34]

$$l \simeq 10^{-8} \mu (m^*/m)^{1/2} ,$$

where m is the mass of the electron. In the case of electronic semiconductors the mean free path has been shown[33,34] to lie between 10^{-9} and 10^{-4} cm. In these materials the interatomic distances are $r \cong (3-5) \times 10^{-8}$ cm, and the wave length of

the free electrons and holes moving with thermal velocity at room temperature is $\lambda \cong 7 \times 10^{-7}$ cm. It is found that $l < \lambda$ for all semiconductors with a mobility $\mu < 100$ cm^2 V^{-1} s^{-1}, and $l < r$ for $\mu < 5$ cm^2 V^{-1} s^{-1}. However, free motion of the carriers at some average velocity is possible only at a distance l. Therefore it is clear that the concept of a carrier velocity becomes meaningless for all semiconductors with $\mu < 100$ cm^2 V^{-1} s^{-1}.[33,34] As Ioffe and Regel' have pointed out, the mean free path and the mobility of the charge carriers also become meaningless for semiconductors in which $l < \lambda$ (and especially when $l < r$), since in the quantum-mechanical model the electron is "smeared out" over a region of length λ.

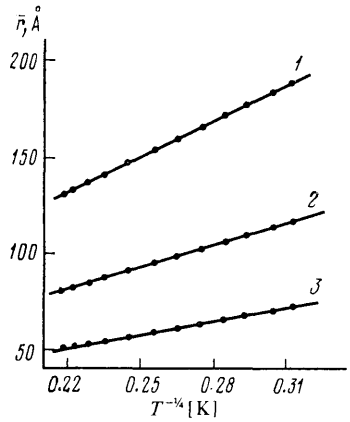


Figure 4. Temperature dependence of the average jump length of the charge carriers in PAN semiconducting pyropolymers heat treated at: *1*) 400°, *2*) 500°, and *3*) 600°.[75]

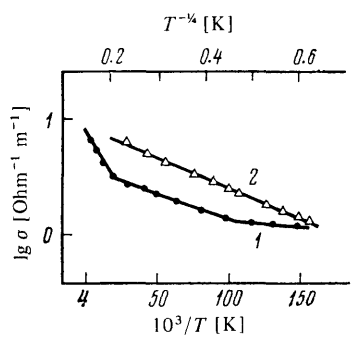


Figure 5. Temperature dependence of the electrical conductivity of a copolymer of cyano-acetylene and acetylene, plotted as: *1*) lg σ against T^{-1} (after Ref.6), and *2*) lg σ against $T^{-1/4}$.

In their treatment of the charge transport phenomenon as a special type of chemical reaction with an activation energy E Ioffe and Regel' expressed the temperature dependence of the carrier mobility (for low applied electric fields) as

$$\mu \propto \exp(-E/k_B T).$$

According to this expression the parameter μ increases exponentially with temperature in semiconductors with a low mobility of charge carriers. A low mobility, increasing with temperature, is consistent with an activational mechanism for the transfer of charge carriers through potential barriers.

The work described in Refs.32–34 laid the foundations for the development of extensive studies of the physical properties of disordered systems, such as amorphous or liquid semiconductors, in which the short-range structural order plays the key role in the formation of the electron energy spectrum and determines the localisation of the electronic states attending an increase in the structural disorder factor[42]. It has been suggested[33,34] that in low-mobility semiconductors the term "mobility" should be replaced by the concept of a frequency of transitions between localised states. The results discussed above show that an increase in temperature increases the frequency of the transition (the transition probability) of the charge carriers between the polyconjugation regions and between their clusters in semiconducting pyropolymers.

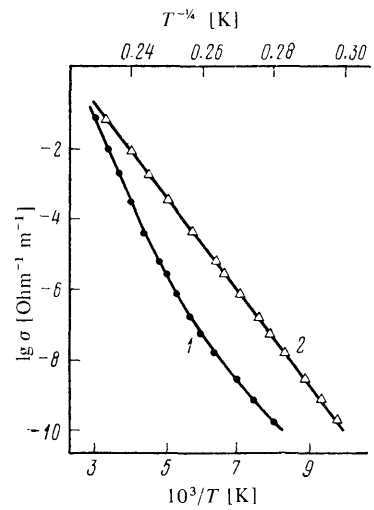


Figure 6. Temperature dependence of the electrical conductivity of thermally- and radiation-modified polyethylene, heat treated at 445° and exposed to iodine at 240°: *1*) plotted as lg σ against T^{-1}, *2*) same data, plotted as lg σ against $T^{-1/4}$.

The above interpretation of the temperature dependence of electrical conductivity applies to all semiconducting polymers. As an illustration we have plotted a large amount of published data[6,7,72,73] according to Mott's law [Eqn.(20)]. As Figs.5–8 show, the curves of electrical conductivity against temperature are linearised in many cases when plotted as lg σ against $(1/T)^{1/4}$.

We should stress that the presence of empty donors is a necessary condition for hopping conduction: in the case of semiconducting pyropolymers free sites must be available in the blocks or in the polyconjugation regions. This condition implies compensation in the semiconductor[35,36]. Hence, the report[77] that the formation of semiconducting pyropolymers is accompanied by substantial compensation appears to be correct.

In conclusion we should note that in our model the density of localised state is independent of energy. In this model the region in which Mott's law (20) applies has neither an upper nor a lower temperature limit[36]. As we see from Figs.2 and 6–8, Mott's law is obeyed over a wide temperature range (10–600 K). Hence we may conclude that in semiconducting pyropolymers the density of states may be treated as constant over a wide temperature range.

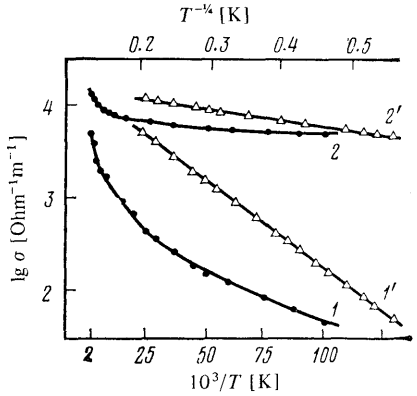


Figure 7. Temperature dependence of the electrical conductivity of PAN thermolysed at *1*) 800° and *2*) 850°: *1*) and *2*) after Ref.72, plotted as lg σ against T^{-1}, *1'*) and *2'*) same data, plotted as lg σ against $T^{-1/4}$.

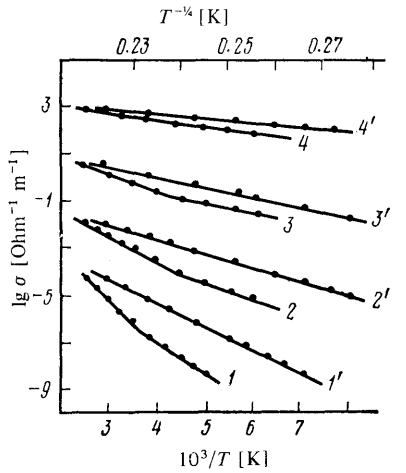


Figure 8. Temperature dependence of the electrical conductivity of PAN thermolysed at *1*) 400°, *2*) 500°, *3*) 600°, and *4*) 700°: *1*), *2*), *3*), and *4*) after Ref.73, plotted as lg σ against T^{-1}; *1'*), *2'*), *3'*), and *4'*) same data, plotted as lg σ against $T^{-1/4}$.

Thus, from the standpoint of a concrete structural model the semiconducting pyropolymers can be divided into three groups. The first group includes the semiconducting pyropolymers in which polyconjugation regions at different distances are gradually converted (as the thermolysis temperature is increased) from isolated states into a state which can support weak exchange interactions, without formation of a joined, continuous phase. Under these conditions the Gaussian shape of the ESR line changes to a mixed shape: Lorentzian in the centre, Gaussian at the tails, and showing a saturation effect. The concentration by volume of polyconjugation regions is ~40–50% towards the upper limit of the formation temperatures of the semiconducting pyropolymers, which depends on the nature and structure of the initial component as well as on the thermolysis conditions. In the case of PAN the semiconductors prepared by thermolysis below 600° belong to the first group. According to our model the materials in this group (which have a fairly high resistance) can be treated as two-component systems in which the polyconjugation regions (or their clusters) behave as electrically conducting inclusions while the insulating component forms the continuous matrix. The distance between polyconjugation regions, i.e. the thickness of the poor conductor, has a real physical significance and determines the height of the potential barrier opposing the motion of the current carriers.

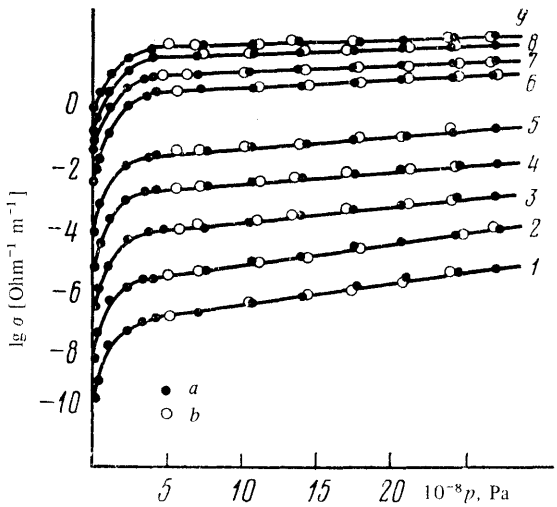


Figure 9. Electrical conductivity σ against pressure p for powdered PAN semiconductors prepared at: *1*) 400°, *2*) 450°, *3*) 500°, *4*) 550°, *5*) 600°, *6*) 650°, *7*) 700°, *8*) 750°, and *9*) 800°; (*a*) and (*b*) denote increasing and decreasing pressure runs respectively.

The second group consists of the semiconducting pyropolymers prepared at temperatures corresponding to extrema in the dependence of the number of PMC on the thermolysis temperature. The ESR line of these semiconductors is Lorentzian, and does not show a saturation effect. In the preparation of PAN semiconductors this temperature region is found between 600 and 700° (Table 1). The samples prepared at these temperatures can be described as a random mixture of a conducting and an insulating component, both components forming continuous phases. In other words, at the lower end of this range of formation temperatures the conducting component just begins to form an infinite cluster, i.e. for temperatures $T_{form} \geq 600°$ we have $V_1 > V_c$. This conclusion is confirmed by the low value of the activation energy for conduction for relatively high values of the resistivity[53]. The *S* values for these samples (denoted by an

asterisk in Table 1) are physically meaningless: they define the effective distances between polyconjugation regions for samples in which these regions are uniformly embedded in a poorly conducting matrix.

The third group includes the semiconducting pyropolymers with strong interactions between the polyconjugation regions, which occupy most of the available volume and form a continuous phase (infinite cluster). Pyropolymers of this group are formed at temperatures above the level corresponding to a decrease in the number of PMC with increase of T_{form}. Materials in this group can be treated as matrix systems, the matrix consisting of polyconjugation regions developed in three dimensions with random microscopic inclusions of a resistive component, whose volume fraction decreases as T_{form} increases. The resistive inclusions could be dielectric impurities, defects, and pores, formed during the thermolysis of the initial polymer. In these samples the distance between resistive inclusions is more meaningful than the parameter S. If the number of resistive inclusions is of the same order as the number of PMC the distance between the inclusions is of the same order as the parameter L.

We should note that the transition of semiconducting pyropolymers between these groups occurs at temperatures depending on the structure of the initial polymer and on the pyrolysis conditions. For example, inorganic substrates can lower the transition temperature of PAN semiconductors by 100–150 K.[78]

III. PRESSURE DEPENDENCE OF THE ELECTRICAL CONDUCTIVITY

If the above heterogeneous models of the structure of semiconducting pyropolymers are correct the dependence of the electrical conductivity (σ) on pressure (p) should become less marked as the pyrolysis temperature of the polymer increases, i.e. as the concentration of polyconjugation regions in the sample increases, because the latter are denser than the resistive layers between them. In other words, for the three groups of semiconducting pyropolymers defined above the pressure sensitivity should decrease in the order group I > group II > group III. This conclusion will prove correct only if the height of the potential barriers between the regions of delocalised electrons[79,80] is affected by the pressure.

Studies of the effect of pressure on the electrical conductivity of semiconducting pyropolymers are needed not only to provide an answer to this type of question but also to establish the possibility of using these materials as the sensitive element of pressure transducers, and to allow for contact phenomena between the particles of powdered samples in the measurement and interpretation of their electrical properties. The latter aspect is quite important, because many semiconducting polymers are available only as powders which cannot be pelleted. Therefore it important to know the pressure at which the powdered sample behaves as a monolithic sample, and the way to determine the electrical parameters corresponding to the monolithic state at $p \to 0$ (or at atmospheric presure), so as to obtain the electrical conductivity of individual particles of the powder.

The effect of hydrostatic compression on the electrical conductivity and thermo-electric power of PAN fibre heat-treated at 600 and 650° has been reported[79,80]. Powdered samples are thought[79] to be unsuitable for this work, because their resistance depends on contacts between particles, whereas fibres behave as monolithic specimens. However, fibres cannot be used to study carrier transport over a wide range of pressure, because they break at loads >8 kbar.[1] We have therefore studied[81,82] the effect of quasi-hydrostatic pressures between atmospheric and 30 kbar on the electrical conductivity parameters of powdered semiconducting pyropolymers based on PAN and thermolysed at 300–900°. This work has produced convincing answers to some of the questions formulated above, and will be reviewed in some detail.

In Fig.9, taken from Ref.82, two regions can be distinguished: in the first σ rises very steeply as p is raised to 3.4×10^8 Pa, suggesting densification of the powdered sample and an increase in the area of contact between the particles. We know[83] that the average porosity of a compressed powder decreases monotonically as a function of the applied pressure, and vanishes at a specific pressure, when the density and the conductivity of the sample become equal to those of the individual particles of the power. We see from Fig.9 that for heat-treated PAN powders this pressure lies in the region of 3500–4000 kg cm^{-2}. Beyond these pressures we observe the second region, in which the experimental points (plotted as lg σ against p) are almost indistinguishable from the straight lines

$$\sigma = \sigma_{p=0} \exp\left(\frac{ap}{k_B T}\right), \qquad (27)$$

where a is a constant.

Table 5. Dependence of $\sigma_{p=0}$ and of the parameter a on the heat treatment temperature (T_{form}) of PAN.[82]

T_{form}, °C	$\sigma_{p=0}$, Ohm^{-1} cm^{-1}	$10^{-4}a$, eV cm^2 kg^{-1}	T_{form}, °C	$\sigma_{p=0}$, Ohm^{-1} cm^{-1}	$10^{-4}a$, eV cm^2 kg^{-1}
400	$3.97 \cdot 10^{-10}$	4.2	650	$3.97 \cdot 10^{-3}$	1.1
450	$1.41 \cdot 10^{-8}$	3.68	700	$1.58 \cdot 10^{-1}$	0.9
500	$6.25 \cdot 10^{-7}$	2.65	750	$8.85 \cdot 10^{-1}$	0.6
550	$1.77 \cdot 10^{-5}$	1.84	800	1.77	0.36
600	$2.94 \cdot 10^{-5}$	1.69			

The pre-exponential term $\sigma_{p=0}$ for a monolithic sample corresponds to the electrical conductivity in the absence of pressure[79]. In the case of a powdered sample $\sigma_{p=0}$ defines the electrical conductivity at zero pressure but assumed independent of the contact between the particles, i.e. $\sigma_{p=0}$ corresponds to the monolithic state of the powder at $p = 0$. The true value of $\sigma_{p=0}$ for a powder is determined by extrapolating to $p = 0$ the linear portion of the lg σ against p plot. Values of $\sigma_{p=0}$ obtained in this way and values of a calculated by Eqn.(27) for PAN samples heat-treated at different temperatures are given in Table 5 (taken from Ref.82). As T_{form} is increased the constant a decreases, and $\sigma_{p=0}$ increases. This quantity is identical to the value $\sigma_{20°}$ obtained from the plots of lg σ against T^{-1} at a pressure of 3500 kg cm^{-2}. Hence, and in the light of the above definition of $\sigma_{p=0}$, we can write

$$\sigma_{p=0} = \sigma_3 \exp\left(-\frac{\varepsilon_3}{k_B T}\right), \qquad (28)$$

where ε_3 is the thermal activation energy for conduction at zero pressure. Thus Eqn.(28) describes the temperature dependence of the hopping conduction in the constant activation energy regime at zero pressure.

From formulae (27) and (28) we obtain the following expression for the temperature dependence of the electrical conductivity in the presence of an applied pressure:

$$\sigma = \sigma_3 \exp\left(-\frac{\varepsilon_3 - ap}{k_B T}\right). \qquad (29)$$

It follows from this expression that a is a quantity (depending on the nature of the sample) which describes the decrease in the activation energy for electrical conduction in semiconducting pyropolymers brought about by the application of unit pressure, i.e.

$$\varepsilon_3'-\varepsilon_3''=-a(p_1-p_2) \quad \text{or} \quad \Delta\varepsilon=-a\Delta p\,, \tag{30}$$

where ε_3' and ε_3'' are the activation energies for conduction at pressures p_1 and p_2 respectively. As Table 6 shows[82], the activation energy for conduction decreases linearly with increase of pressure, as required by Eqn.(30). Extrapolation to zero pressure gives the activation energy for conduction in the "monolithic" state of the powder in the absence of pressure. The activation energies for conduction obtained in this way are 0.01–0.02 eV lower than the values for powder samples densified by vibration.

Table 6. Electrical conductivity parameters of heat-treated PAN at different pressures.

$10^3\,p$, kg cm^{-2}	T_{form} = 400 °C			T_{form} = 550 °C			T_{form} = 700 °C		
	$\sigma_{20°C}$, Ohm^{-1} cm^{-1}	σ_{ε_3}, Ohm^{-1}cm^{-1}	ε_3, eV	$\sigma_{20°C}$, Ohm^{-1}cm^{-1}	σ_{ε_3}, Ohm^{-1}cm^{-1}	ε_3, eV	$\sigma_{20°C}$, Ohm^{-1}cm^{-1}	σ_{ε_3}, Ohm^{-1} cm^{-1}	ε_3, eV
0.001*	$1.41\cdot10^{-12}$	$7.80\cdot10^{-6}$	0.39	$4.17\cdot10^{-8}$	$1.33\cdot10^{-3}$	0.26	$3.57\cdot10^{-4}$	$6.3\cdot10^{-2}$	0.13
4.00	$7.04\cdot10^{-10}$	$1.76\cdot10^{-3}$	0.37	$2.24\cdot10^{-5}$	$4.7\cdot10^{-1}$	0.25	$1.77\cdot10^{-1}$	14.1	0.11
10.80	$2.32\cdot10^{-9}$	$1.82\cdot10^{-3}$	0.34	$4.17\cdot10^{-5}$	$3.94\cdot10^{-1}$	0.23	$2.24\cdot10^{-1}$	12.0	0.10
18.00	$7.61\cdot10^{-9}$	$1.74\cdot10^{-3}$	0.31	$6.10\cdot10^{-5}$	$3.84\cdot10^{-1}$	0.22	—	—	—
21.40	$1.26\cdot10^{-8}$	$1.95\cdot10^{-3}$	0.30	$8.9\cdot10^{-5}$	$3.80\cdot10^{-1}$	0.21	$3.71\cdot10^{-1}$	13.4	0.09

*These data refer to a powder densified by vibration in a quartz cylinder at atmospheric pressure.

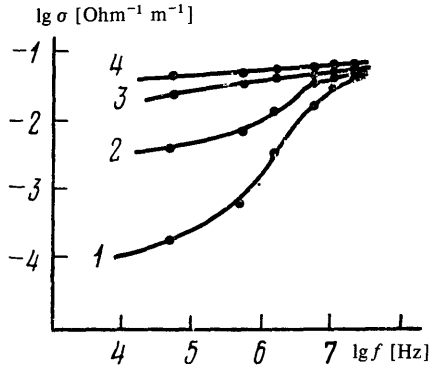


Figure 10. A.c. conductivity against frequency at different pressures for a sample of PAN heat treated at 600°: *1*) atmospheric pressure, *2*) 1.0×10^3, *3*) 3.5×10^3, *4*) 1×10^4 kg cm^{-2}.[82]

We would stress that in the linear region of the plots of lg σ against p the change of σ with pressure is reversible (see Fig.9), and therefore in this region (at $p \geq 3500$ kg cm^{-2}) the properties of the powdered semiconducting pyropolymer samples are indistinguishable from those of monolithic specimens. Measurements of the a.c. conductivity under pressure have confirmed this view. Since the conductivity of a fibre (monolithic specimen) of thermolysed PAN is independent of frequency[79], the gradual decrease in the frequency dependence of conductivity with increase of pressure (Fig.10) confirms the above conclusion.

In 1960 Tal'roze and Blyumenfel'd[84] observed a linear dependence of lg σ_3 on ε_3 (i.e. a compensation effect) in a wide range of polymeric semiconductors. A detailed analysis of various aspects of this phenomenon from the point of view of the chemical physics of the solid state is given in Ref.85. As Fig.11 shows, a linear relationship is observed also between lg $\sigma_{p=0}$ and a, which vary in opposite senses, i.e. according to the equation

$$a=b+c\lg\sigma_{p=0} \tag{31}$$

whose coefficients b and c (calculated by least squares) are 0.456×10^{-6} and -0.382×10^{-6} respectively.

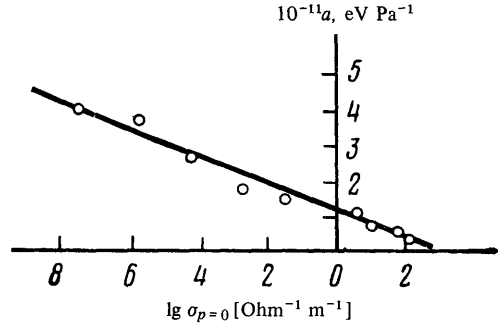


Figure 11. Pre-exponential factor $\sigma_{p=0}$ in Eqn.(27) against the constant a for heat-treated PAN samples[82].

From the lack of dependence of the pre-exponential factor σ_3 on p in the linear part of the lg σ(p) function (see Fig.9 and Table 6) and from the inverse variation (31) between $\sigma_{p=0}$ and a we may conclude that the main effect of pressure is an increase in the mobility of the charge carriers, the concentration of the carriers being unaffected by the pressure. The same conclusion was reached[80] from an observation of the pressure-independence of the thermo-electric power of pyrolysed PAN fibre, coupled with a decrease in the activation energy for electrical conduction with increase of pressure.

However, we should point out that Shimamura and coworkers[86,87] concluded from a study of the electrical conductivity of polyacetylene at pressures up to 108 kbar between room temperature and liquid-nitrogen temperature that the concentration of current carriers increases with pressure. This conclusion is incorrect, because the pre-exponential factor is sensitive to changes in the density of charge carriers[4], and therefore constancy of this factor coupled with a decrease in the activation energy for conduction with increase of pressure implies that the main influence of pressure on the electrical conductivity of polymeric semiconductors is to increase the mobility of the carriers by lowering the potential barriers.

From Tables 5 and 6 and Fig.9 we note that the pressure dependence of the electrical conductivity decreases as T_{form} increases, i.e. as the volume concentration of polyconjugation regions increases. These results indicate that the structural features of the pyropolymers and their changes with thermolysis temperature are correctly reflected, on the whole, by the heterogeneous models discussed above. They also show that the main effect of pressure is on the potential

barriers which separate the regions containing delocalised electrons. In other words, the insulating inter-layers are more compressible than the polyconjugation regions. The semiconducting pyropolymers of group I are the more pressure-sensitive, and they can be used as the sensing element in pressure transducers. A detailed analysis of the advantages of polymeric semiconductors as materials for pressure transducers will be found in Ref.88.

IV. RELATIONSHIP BETWEEN THE NUMBER OF PARAMAGNETIC CENTRES AND THE ELECTRICAL CONDUCTIVITY

A large volume of work, reviewed in Refs.1, 2, and 7, suggests the existence of a definite relationship between the electrical and the paramagnetic properties of polymeric semiconductors. However, different points of view have been put forward in the interpretation of this phenomenon. For example, some workers[89,90] consider that at high enough levels of conjugation (i.e. under conditions of eka-conjugation) the electronically excited state can exist at room temperature because the distance between the ground and the triplet state is small, and charge carriers formed by the scheme

$$R + \ddot{R} \rightleftarrows R^+ + R^-$$

are recorded in the ESR spectra. The authors[89,90] used the theory of rate processes to explain the relationship between conductivity and paramagnetism in polymers with conjugated bonds.

Vlasova and coworkers[91,92] conclude from the good agreement between experimental values of the thermoelectric power of thermolysed PAN and polypyridine and the values calculated by the band theory of solids that the PMC behave as donor impurities in these materials. This work suggests (implicitly) that the unpaired electrons transferred to the conduction band by the ionisation of the donors give the same ESR signal as the electrons still in the filled donors[2]. Further work is needed to confirm this conclusion.

An analysis of the electrical and paramagnetic characteristics of polymeric semiconductors led Vannikov and Boguslavskii[2] to conclude that in most cases a direct link between the electronic states which control the electrical and the paramagnetic properties cannot be established. If such a link exists, it can only be discovered by detailed studies and comparisons of the electrical and paramagnetic properties over a wide range of experimental conditions and of chemical composition and structure of the sample[2]. We note in this connection the work of Volod'ko and coworkers[93], who obtained an expression directly relating the electrical conductivity and the number of PMC by using the hopping model of conduction. According to that model the mobility is expressed by the formula[4]

$$\mu = \frac{fSeN_s(k_BT)}{h^3\nu^2}\exp\left(-\frac{\varepsilon_s}{k_BT}\right), \qquad (32)$$

where f is the average angle between the jump direction and the vector of the electric field, S is the distance between molecules, N_S is the number of neighbouring molecules, ν is the vibration frequency of the activated complex in a plane normal to the direction of motion of the charge carriers, ε_S is the height of the barrier, and h is Planck's constant. In the case of semiconducting pyropolymer S is interpreted as the distance between polyconjugation regions, and N_S as the number of adjacent polyconjugation regions.

Eqn.(32) has no practical applications, because it contains quantities which cannot be measured experimentally. Therefore, introducing the substitutions

$$S=\xi_1 N^{-1/3};\ f=a_0N^{1/3}/\xi_1;\ N_s=R^3N;\ \varepsilon_s=\varepsilon_3;\ \nu=\varepsilon/h;\ n=N\xi, \qquad (33)$$

where a_0 is the mean radius of the molecule, R is the mean intermolecular interaction radius, ξ is a quantity depending on N, ξ_1 is a constant, and ε_3 is the activation energy for hopping conduction, Volod'ko and coworkers[93] obtained from (24) and (32) the expression

$$\sigma=\alpha_1\varphi(N)N^{5/3}(k_BT/\varepsilon_3)^2\exp\left(-\frac{\varepsilon_3}{k_BT}\right), \qquad (34)$$

where $\phi(N)$ is a function of N, and

$$\alpha_1=e^2a_0\xi_1R^3/\hbar. \qquad (35)$$

Formula (34) accurately describes the electrical conductivity of polymers with a polyconjugated system if the following condition applies[93]:

$$\varphi(N)=\varphi_0\exp\left(-\beta\frac{N^{1/3}}{\gamma+N^{1/3}}\right). \qquad (36)$$

Inserting (36) into (34) gives

$$\sigma=\alpha N^{5/3}\left(\frac{k_BT}{\varepsilon_3}\right)^2\exp\left[-\frac{\varepsilon_3}{k_BT}-\beta\frac{N^{1/3}}{\gamma+N^{1/3}}\right], \qquad (37)$$

where $\alpha = \alpha_1\phi_0$, β, and γ are constants; the values $\ln\alpha = -44.7$, $\beta = 40$, and $\gamma = 1.3\times10^6$ were obtained[93] by least squares.

Satisfactory agreement was obtained in a comparison[93] of experimental electrical conductivity data for 44 polymeric semiconductors with the values calculated by formula (37). Differences of an order of magnitude between calculated and experimental conductivities are ascribed to errors in the measurement of the activation energy for conduction and of the concentration of PMC. However, in some samples discrepancies as high as 1.4–7 orders of magnitude were obtained[93]: no attempt was made to explain these large errors.

In spite of the satisfactory results given by formula (37) for most of the materials studied by Volod'ko and coworkers[93], the extent to which this formula is universal remains to be established. To solve this problem we need first of all to demonstrate the universality of the constants α, β, and γ which appear in formula (37), and the lack of dependence of the results upon the type of interaction between the PMC.

Comparing the first of the substitutions (33) with Eqn.(7) we can write, for the case of semiconducting pyropolymers,

$$\xi_1=1-V_1^{1/3}=1-LN^{1/3}, \qquad (38)$$

i.e. ξ is the linear fraction of dielectric inter-layers between polyconjugation regions. Inserting (38) into (35) we obtain

$$\alpha=\frac{e^2a_0(1-V_1^{1/3})R^3}{\hbar}\varphi_0=\frac{e^2a_0(1-LN^{1/3})R^3}{\hbar}\varphi_0. \qquad (39)$$

In the case of semiconducting pyropolymers a_0 and R are interpreted as $L/2$ and $S/2$ respectively, i.e. within the definition of the structure parameters given in Section II $a_0 = L/2$ and $R = S/2$. Hence, when applied to semiconducting pyropolymers Eqn.(39) becomes

$$\alpha=\frac{e^2L(1-V_1^{1/3})S^3}{16\hbar}\varphi_0. \qquad (40)$$

Clearly, the quantity α depends on the nature and on the structure parameters of the polymeric semiconductor, i.e. it takes a different value for each polymer. Therefore the use[93] of a single value (ln

($\ln\alpha = -44.7$) to calculate the electrical conductivity of polymeric semiconductors by Eqn.(37) is unjustified. This is

probably one of the main reasons for the discrepancy between experimental conductivities and those calculated by Eqn.(37). Nothing has been said about the universality of the constants β and γ, since there is no physical justification for the choice of the function (36), which appears to have been purely empirical. Nevertheless this function shows how complex is the relationship between the concentration and mobility of the charge carriers and the number of PMC in the polymer.

The reason why formula (37) with the constants α, β, and γ given in Ref.93 can be used for semiconducting pyropolymers according to the nature of the interactions between PMC was discussed in Ref.54. It was shown that the electrical conductivity of semiconducting pyropolymers of group I (see Section II), in which the polyconjugation regions and their clusters do not merge into a continuous phase, i.e. in which the interaction between these regions are weak, are most accurately described by formula (37). The largest deviations occur with samples from group II, prepared at temperatures corresponding to extrema in the dependence of the number of PMC on the thermolysis temperature of the initial polymer. The same conclusion follows from Eqn.(40), since in semiconductors of groups II and III the parameter S has no real physical meaning (see Section II).

To conclude this Section we should stress the following aspect. By comparing Eqn.(29) for $p = 0$ with Eqn.(37) we obtain

$$\sigma_3 = \alpha N^{5/3} \left(\frac{k_B T}{\varepsilon_3}\right)^2 \exp\left(-\frac{\beta N^{1/3}}{\gamma + N^{1/3}}\right) . \qquad (41)$$

Though this comparison of the universal (over a narrow temperature range) equation (29) at $p = 0$ with an expression [Eqn.(37)] whose universality remains to be proved is not entirely justified, it nevertheless allows us to highlight some special features of the quantities ϕ_3, α, β, and γ. Eqn.(41) relates the pre-exponential factor ϕ_3 (which appears in formula (19) for the hopping conductivity in the constant activation energy regime) to the number of PMC. Hence, the relationship between the electrical conduction and the paramagnetic characteristics of semiconducting pyropolymers takes place mainly through the parameter ϕ_3.

We have shown (see Section III) that in the region of reversible pressure effects on the conductivity the pre-exponential factor ϕ_3 in Eqn.(29) is independent of pressure. From this we may conclude that the effects of pressure on the quantities which appear in Eqn.(41) must be mutually compensating. The activation energy for conduction decreases as the pressure increases, in accordance with Eqn.(30). It is evident from Eqn.(40) that the quantity α also should decrease with pressure, since it is proportional to S^3, where S is the thickness of the resistive layers between polyconjugation regions, to which the pressure is effectively applied. The changes in α and in ε_3 brought about by pressure may largely cancel out. A change of N with pressure seems unlikely in the region of reversible pressure dependence of the electrical conductivity of semiconducting pyropolymers. Therefore we are led to the conclusion that β and γ are unaffected by pressure, or that their pressure changes are mutually compensating.

V. CONCLUSIONS

Research into the preparation, properties, and applications of micro-heterogeneous semiconducting pyropolymers may develop in a number of new directions. The structural models of these polymers discussed above suggest the possibility of modifying their properties merely by controlling the degree of interaction between the polyconjugation regions in the system. The gradual change in properties of the initial polymer caused by increasing the thermolysis temperature can be classified as a thermal modification process. However, controlled changes in the properties of semiconducting pyropolymers by the addition of various compounds are also possible. For example, the controlled modification of the paramagnetic and of the adsorption properties of PAN semiconductor pyropolymers by doping with anthracene has been demonstrated[94-96]. The effect of additions of nickel during the pyrolysis of PAN on the electrical properties of the product has been investigated[97,98]. Metal-containing polymeric semiconductors of this type are potentially interesting as selective catalysts based on polyconjugated matrices, and also as materials for switching applications.

We believe that one of the most promising new developments will be the modification of fillers by semiconducting pyropolymers. This area of work includes methods of controlling the grafted polymerisation of acrylonitrile, vinyl acetate, and vinyl chloride on the surface of ordinary cheap fillers. Heat treatment of fillers modified in this way should give electrically conducting fillers for plastics with entirely new properties[99-103]. The work must include a study of the formation of semiconducting pyropolymers on the surface of cheap mineral filler particles, and of the effect of the fillers modified in this way on the physicochemical properties of the polymeric binders. All these problems need to be studied in detail.

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