(Translated into Russian), Inostr. Lit., Moscow, 1961.
11. O. Erbacher, Z. phys. Chem., 164, 135 (1933).
12. O. Erbacher, Z. phys. Chem., A 156, 142 (1931).
13. O. Erbacher, Z. phys. Chem., 182, 256 (1938).
14. N. Hackerman and S. Stephans, J. Phys. Chem., 58, 904 (1954).
15. K. E. Heusler and G. H. Cartledge, J. Electrochem. Soc., 108, 732 (1961).
16. Z. A. Iofa and G. V. Rozhdestvenskaya, Dokl. Akad. Nauk SSSR, 41, 1159 (1953).
17. L. A. Medvedeva and Ya. M. Kolotyrkin, Zhur. Fiz. Khim., 31, 2668 (1957).
18. Ya. M. Kolotyrkin and L. A. Medvedeva, Dokl. Akad. Nauk SSSR, 140, 168 (1961); 143, 1384 (1962).
19. K. Schwabe, K. Wagner, and C. Weissmantel, Z. phys. Chem. (Leipzig), 206, 309 (1957).
20. K. Schwabe, Chem. Tech. (Berlin), 10, 469 (1958).
21. K. Schwabe, Chem. Tech. (Berlin), 13, No. 5 (1961).
22. K. Schwabe, Isotopen Tech., 1, 175 (1960–1961).
23. K. Schwabe and W. Schwenke, Electrochim. Acta, 9, 1003 (1964).
24. I. A. Kafalas and H. C. Gatos, Rev. Sci. Instr., 29, 47 (1958).
25. J. O'M. Bockris, Z. phys. Chem. (Leipzig), 214, 1 (1960).
26. E. Blombgren and J. O'M. Bockris, Nature, 186, 305 (1960).
27. A. Slygin, A. Frumkin, and W. Medwedowsky, Acta Physicochim. URSS, 4, 911 (1936); 3, 791 (1935).
28. N. A. Balashova and N. S. Merkulova, Symposium "Novye Metody Fiziko-Khimicheskogo Issledovaniya, Trudy Inst. Fiz. Khim. Akad. Nauk SSSR" (New Methods of Physicochemical Investigation, Transactions of the Institute of Physical Chemistry of the Academy of Sciences of the USSR), Izd. Akad. Nauk SSSR, Moscow, 1957, No. 6.
29. V. E. Kazarinov and N. A. Balashova, Pered. Nauch. Tekh. Opyt, Inst. Nauch. i Tekh. Inform., No. 17-63-883/7, 7, p. 18 (1963).
30. V. E. Kazarinov and N. A. Balashova, Dokl. Akad. Nauk SSSR, 157, 1174 (1964).
31. V. E. Kazarinov, Candidate's Thesis, Institute of Electrochemistry of the Academy of Sciences of the USSR, Moscow, 1962.
32. W. E. Kasarinov, Z. phys. Chem. (Leipzig), 226, 167 (1964).
33. N. A. Balashova and A. N. Frumkin, Dokl. Akad. Nauk SSSR, 20, 449 (1938).
34. B. Erschler, Acta Physicochim. URSS, 7, 327 (1937).
35. A. D. Obrucheva, Zhur. Fiz. Khim., 32, 2155 (1958).
36. N. A. Balashova and M. I. Kulezneva, Elektrokhimiya, 1, 155 (1965).
37. A. Kasawa, J. Electrochem. Soc., 110, 174 (1963); J. Electroanalyt. Chem., 8, 20 (1964).
38. L. Müller and V. V. Sobol', Elektrokhimiya, 1, 111 (1965).
39. V. E. Kazarinov and N. A. Balashova, Dokl. Akad. Nauk SSSR, 139, 640 (1961).
40. N. A. Balaschova, Wiss. Z. tech. Univ., Dresden, 12, 1177 (1963).
41. A. N. Frumkin and A. Titievskaya, Zhur. Fiz. Khim., 31, 485 (1957).
42. A. N. Frumkin and N. Polyanovskaya, Zhur. Fiz. Khim., 32, 157 (1958).
43. "Surface Phenomena in Chemistry and Biology", Pergamon Press, London, 1958, p. 189.
44. A. D. Obrucheva, Dokl. Akad. Nauk SSSR, 120, 1072 (1958).
45. A. D. Obrucheva, Dokl. Akad. Nauk SSSR, 142, 859 (1962).
46. A. N. Frumkin, Adv. Electrochem. Electrochem. Eng., 3, 287 (1963).

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ORGANIC SEMICONDUCTORS BASED ON POLYETHYLENE

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I. INTRODUCTION

The earliest observations of properties characteristic of semiconductors in organic compounds were made with some polynuclear hydrocarbons and dyestuffs. Studies of the electrophysical properties of various compounds as a function of their structure led to the conclusion that semiconductor properties arise when a sufficiently well-developed system of conjugated double bonds is present in the molecules. This problem has been the object of many investigations, and has been discussed in a number of review articles [1-3]. It is now well established that organic polymers as well as low-molecular-weight compounds can exhibit semiconductor properties. This widens the scope of possible applications, since the synthesis of polymers with technologically desirable mechanical properties offers the advantages of controlled structure and controlled properties.

Polymeric semiconductors can be prepared either by synthesis from monomers which offer the necessary system of conjugated bonds, or by inducing polyconjugation into the complete polymers by one of several methods. In the former case the possibilities of generating polymers of different structures are almost limitless, but the resulting materials are mostly insoluble and infusible powders, and their molecular weight is not very high. It is possible also to convert a polymeric dielectric gradually into a polymeric semiconductor by radiation-induced structural changes followed by heat treatment. Many studies of the pyrolysis of polymers have been published. The electrophysical properties of the products have been most fully investigated for polyvinylbenzene [4] and polyacrylonitrile [5] for which heat treatment is clearly shown to be a very effective way of raising the conductivity.

Polyethylene is a suitable material for this purpose, because it has a stable polymeric structure and the effect of radiation on it has been studied in detail. It is well known that irradiation develops a structure in polyethylene,

forming 5–7-membered rings with the loss of a significant amount of hydrogen. The basic problem is to find the cross-linking and cyclisation conditions for the linear macromolecules which will lead to the creation of a unified structure, susceptible to subsequent heat treatment, and also to identify the mechanism giving rise to semiconductor properties.

The electrophysical and paramagnetic properties of the products of the radiation-thermal modification of polyethylene (RTMP) have been studied as a function of the dose of radiation absorbed and of the heat-treatment conditions. The following properties have been studied over a wide range of values: the conductivity in a d.c. or a.c. field, its temperature coefficient, the differential thermo-e.m.f., the structure of the products (by ESR and infrared spectroscopy), and lastly the effect of additives and the photoconductivity.

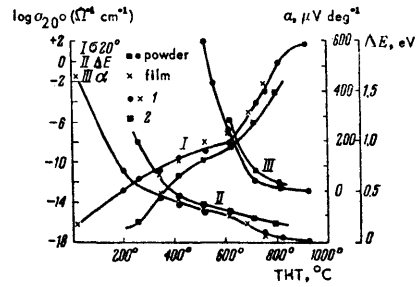


Fig. 1. Variation of electrical characteristics with dose and THT:
1) $D = 2.4 \times 10^4$ Mrad; 2) $D = 1.2 \times 10^3$ Mrad.

II. PROCEDURE

The products of RTMP have been studied in powder form and as films. The films were deposited as already described[6] on glass or quartz substrates carrying deposited gold electrodes. The samples were irradiated in evacuated quartz bulbs (~ 10^{-5} mmHg) with fast electrons (5 MeV) from a U-12 accelerator. The heat treatment of the irradiated samples was by a standard procedure (brief oxidation at 260° followed by pyrolysis in a vacuum[7,8]). The d.c. electrical characteristics of specimens were studied in a vacuum (~ 10^{-5} mmHg).[8] Thin-film specimens were examined in surface or multilayer cells, inserted into a special holder. The electrophysical properties of the specimens in powder form were measured in a cell with platinum disc electrodes, at temperatures between 20° and 150° *in vacuo* and in air, and between 20° and -50° for the experiments on specimens with adsorbed iodine.

The d.c. measurements were made with an E6-3 teraohmmeter or with an MO-47 bridge (for low-resistance specimens). The conductivity in an alternating field was measured with an E 10-2 impedance bridge.

Iodine adsorption was measured gravimetrically on a McBain balance, with a temperature control of ±1°C.

The structural properties of the RTMP products were investigated by ESR on an RE 1301 radio-frequency spectrometer.

III. ELECTRICAL PROPERTIES

Most of the results discussed in the present paper were obtained on RTMP films. The electrophysical properties were studied on samples of polyethylene irradiated with three distinct doses[7]: 1.2×10^3, 6.9×10^3, and 2.4×10^4 Mrad.

Conductivity measurements in the temperature range -25°–150° were in satisfactory agreement with the exponential relationship

$$\sigma = \sigma_0 \exp(-\Delta E/kT).$$

Measurements of differential thermo-e.m.f. showed that the resulting materials are *p*-type semiconductors. Between -50° and 150° the differential thermo-e.m.f. α is independent of the mean specimen temperature within the experimental error. Values of $\sigma_{20°}$, ΔE, and α for specimens in powder and in film form are plotted in Fig. 1 against the temperature of heat treatment (THT) for different doses of radiation.

The figure shows that, by varying the dose and the THT, it is possible to obtain materials for which α varies from 1.5 μV deg^{-1} to values in excess of 500 μV deg^{-1}, $\sigma_{20°}$ varies from 10^{-14} to 10^2 Ω^{-1} cm^{-1}, and ΔE from 1.5 to 0 eV. The preliminary heat treatment has a profound effect on the electrophysical properties of the resulting materials. As can be seen from Fig. 1, prescribed values of $\sigma_{20°}$, ΔE, and α are obtained at lower THT, the higher the dose of radiation absorbed by the specimens. The figure also shows that the electrical characteristics of specimens in film and in powder form are in tolerably good agreement. The electronic nature of the conductivity was demonstrated on low-resistance specimens by electrolysis.

Studies of the voltage–current characteristics of different materials have shown that Ohm's law is obeyed at fields between 1 and 2.5×10^3 V cm^{-1}, and that the plot of current against voltage begins to depart from linearity only at fields $> (2.5–5) \times 10^3$ V cm^{-1} (see Fig. 2).

The results summarised in Fig. 1 indicate that materials of different electrophysical characteristics can be prepared by varying either the dose of radiation (D) or the THT. Furthermore, as we shall show below, the electrical properties of the products of RTM of polyethylene can also be altered significantly by introducing electron-acceptor impurities (oxygen, iodine). Nevertheless, it can be shown that the nature of the observed electrophysical properties is the same for all the materials, and is determined by their structural characteristics. This involves studying the electrophysical properties as a function not of the dose or the THT, which characterise the preparative conditions used, but of a parameter of the material itself, such as $\sigma_{20°}$. Fig. 3 shows the relationship between ΔE, α, and $\sigma_{20°}$ for RTM polyethylene: it is evident that the materials, whether in powder or in film form, obey a common, fairly simple functional relation between ΔE and $\sigma_{20°}$ irrespective of the dose, THT, or added impurities. This leads us to conclude that the conduction mechanism is the same for all the specimens which have been examined, and that the change in electrical characteristics is fundamentally dictated, as will be shown below, by changes in the height of the potential barriers ΔE separating regions of polyconjugation.

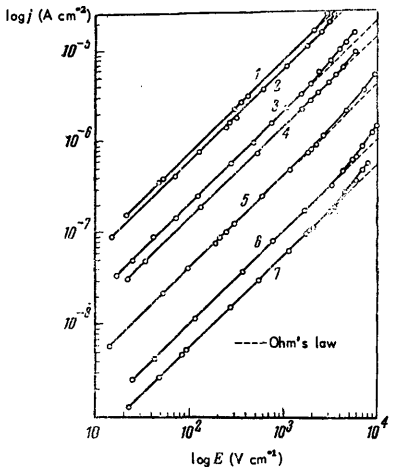


Fig. 2. Current–voltage characteristics of the specimens;
$D = 1.2 \times 10^3$ Mrad: 1) THT = 620°; 6) THT = 520°;
$D = 6.9 \times 10^3$ Mrad: 2) THT = 620°; 4) THT = 520°;
7) THT = 360°;
$D = 2.4 \times 10^4$ Mrad: 3) THT = 530°; 50 THT = 440°.

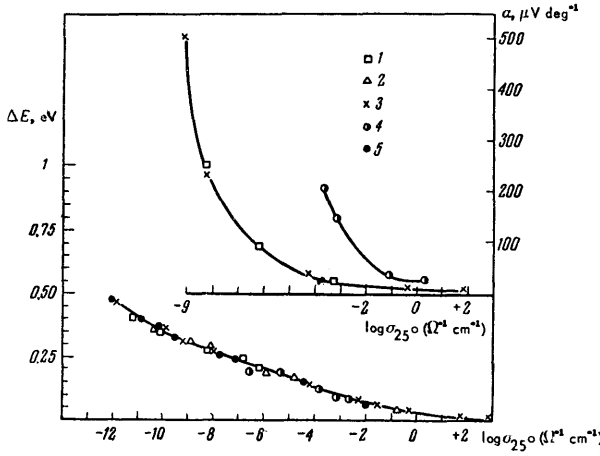


Fig. 3. Relationship between $\sigma_{20°}$, ΔE, and α.
Powders: 1) $D = 1.2 \times 10^3$ Mrad; 2) $D = 6.9 \times 10^3$ Mrad; 3) $D = 2.4 \times 10^4$ Mrad; 4) $D = 2.4 \times 10^4$ Mrad + I_2 at 20°.
Films: 5) $D = 2.4 \times 10^4$ Mrad.

The change in work function of the products of RTMP as a function of THT is of considerable interest. Boguslavskii's measurements[9] of contact potential difference (CPD) of RTMP films with respect to the glass electrode by the vibrating condenser method reveal a systematic lowering in work function with increasing THT. Table 1 gives the values of work function of the films, and also the activation energies for conduction, as a function of THT. The changes in work function and in activation energy for conduction of specimens prepared at different THT, relative to a specimen prepared at a THT of 720°, are also tabulated.

The agreement between the values of ΔE and φ, listed in the last two columns of Table 1, is satisfactory.

TABLE 1.

$D = 2.4 \times 10^4$ Mrad THT, °C	Contact p.d., V	ΔE, eV	φ, V	$\Delta E - \Delta E_{720°}$, eV	$\varphi - \varphi_{720°}$, V
360	+0.16	0.50	5.23	0.35	0.51
510	−0.16	0.33	4.91	0.18	0.19
650	−0.22	0.25	4.85	0.10	0.13
720	−0.35	0.15	4.72	0	0

The frequency dependence (up to 30 Mc/s) of the conductivity of films prepared at different THT has also been investigated[6]: the results are shown in Fig. 4. As a rule, the conductivity increases with increase of frequency and reaches a plateau at 10–20 Mc/s, the frequency at which saturation is reached being lower for the higher THT. For a high-conductivity specimen prepared at a THT of 750°, practically no dispersion of conductivity with frequency is observed. Whereas the d.c. conductivity $\sigma_{20°}$ lies between limits 10 orders of magnitude apart, the conductivity of the same specimens in the region of the plateau (σ_f) at 10–20 Mc/s frequency spans only two orders of magnitude.

The variation of conductivity with frequency has been measured at different temperatures. Fig. 5 shows that higher measurement temperatures lower the frequency at which the conductivity plateau is reached. (These data refer to a THT of 420°.) The increase of conductivity with temperature in the region of the plateau gives an activation energy of $\Delta E_f \simeq 0.05$ eV, whereas the same specimen in a d.c. field has $\Delta E \simeq 0.5$ eV.

The effect of oxygen on the a.c. conductivity has been investigated. In contrast to the d.c. measurements, where oxygen raises the conductivity and lowers the activation

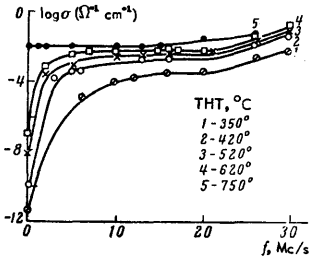


Fig. 4. Frequency dependence of the conductivity of specimens with different THT;
$D = 2.4 \times 10^4$ Mrad.

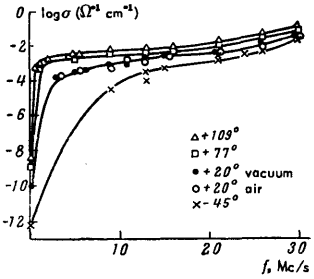


Fig. 5. Variation of conductivity with frequency at different temperatures; specimen with a THT of 440°; $D = 2.4 \times 10^4$ Mrad.

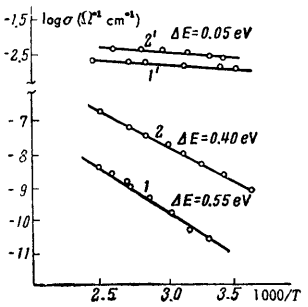


Fig. 6. Temperature dependence of conductivity:
1) and 2) d.c.; 1′) and 2′) 16 Mc/s; 1) and 1′) THT 330°; 2) and 2′) THT 460°.

energy, the conductivity in an a.c. field is quite insensitive to oxygen: Fig. 5 shows that measurements *in vacuo* and in oxygen give identical results.

Fig. 6 shows the temperature variation of the conductivity in a d.c. field and at a frequency of 16 Mc/s (i.e. in the plateau region) for two specimens. It is interesting to compare the values of σ_0 (from measurements in a d.c. field) and σ_f (in the plateau region) for given specimens. As shown in Table 2, σ_0 and σ_f are of the same order of magnitude for all specimens.

In the surface cell film conductivities could be studied up to the temperatures at which the specimens had been prepared, even while the heat treatment was in progress. It was found that conductivity measurements above 250° gave an activation energy for conduction well in excess of the value obtained from measurements between 20° and 150°. Thus, the activation energy calculated from the temperature dependence in the region 20–200° for polyethylene films prepared at a THT of 440° is 0.40 eV, whereas in the temperature range from 250° to 420° the value is 0.90 eV. The corresponding values for specimens with a THT of 520° are 0.30 and 0.75 eV in the low- and the high-temperature region respectively.

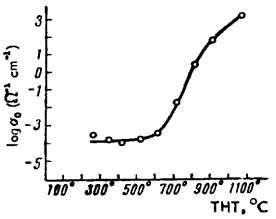


Fig. 7. Variation of σ_0 with THT.

TABLE 2*.

THT, °C	σ_0, Ω⁻¹ cm⁻¹	σ_f, Ω⁻¹ cm⁻¹
350	1×10^{-3}	2.5×10^{-4}
420	1.5×10^{-3}	4×10^{-3}
520	3×10^{-3}	4×10^{-3}
620	5×10^{-3}	6×10^{-3}
760	2×10^{-2}	1×10^{-3}

* The variation of σ_0 with THT is presented in Fig. 7.

Optical and photoelectric effects on RTMP films have been examined[10]. The long-wave absorption edge and the photoelectric sensitivity maximum are both shifted towards the infrared region as the THT is raised.

These observations on the frequency and temperature dependence of the conductivity have led to the hypothesis that the products of RTM of polyethylene have a micro-heterogeneous structure, characterised by regions of high conductivity separated by poorly conducting regions which give rise to the barrier mechanism of current flow.

IV. ELECTRON SPIN RESONANCE

The electron spin resonance (ESR) method has been used to examine the correctness of this hypothesis. ESR studies of the products of radiation-induced and radiation-thermal modification of polyethylene rely on observations of the shape and width of the ESR line, of the saturation effect, and also of the interaction between paramagnetic centres (p.m.c.) and oxygen molecules as a function of the dose of radiation absorbed and temperature of the subsequent heat treatment. According to published results[11,12], ESR detects alkyl radicals ($-CH_2-\dot{C}H-CH_2-$) in polyethylene which has been irradiated with a dose of less than 10 Mrad, allyl radicals ($-CH_2-\dot{C}H-CH=CH-CH_2-$) for doeses of $10-10^{-2}$ Mrad, and linear polyene radicals ($-CH=CH-\dot{C}H-CH=CH-$) if the dose rises to 4×10^3 Mrad. The effect of still higher doses had not been previously investigated. We have found[13,14] that at doses in the region of 6×10^3 Mrad a new ESR line appears, with a width of 7.5 oersted, when the measurements are carried out in the presence of oxygen. The intensity of this line increases with dose.

Material prepared by irradiation of polyethylene to an absorption of 2.2×10^4 Mrad was used to study the effect of subsequent heat treatment. The variation of line-width with THT is shown in Fig. 8: it is clear that the width measured under moderate vacuum remains constant at 7.5 oersted up to a THT of 400°, and at more elevated THT the line-width initially drops to 0.5 oersted (at 720°) before rising again very steeply, reaching 50 oersted at 1100°.

Specimens prepared at temperatures below 450°, and also the original irradiated material without any heat treatment, show a characteristic saturation effect of the ESR line, which gradually vanishes as the THT is raised. It has been shown that the line width does not vary as a result of saturation. It follows that the observed line is not evenly developed, and is the envelope of a set of

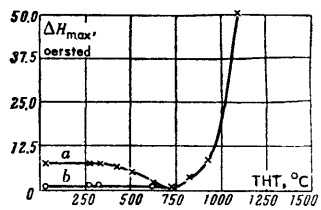


Fig. 8. Variation of ESR line width with THT:
a) 2 h evacuation at 10^{-5} mmHg and 20°;
b) 30 h evacuation at 10^{-6} mmHg and 20°.

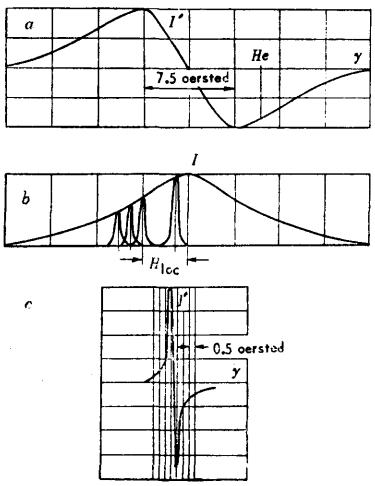


Fig. 9. ESR spectra of materials prepared at THT = 270°:
a) differential form, 2 h evacuation at 10^{-5} mmHg and 20°; *b*) integral form of spectrum *a*; *c*) differential form, 30 h evacuation at 10^{-6} mmHg and 20°.

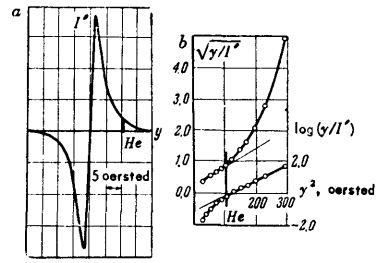


Fig. 10. *a*) ESR spectrum of products obtained at THT = 550°; *b*) linearisations of spectrum *a*.

TABLE 3.

Material	Measurement conditions ΔH_{max}, 10^{-5} mmHg	−196° 10^{-5} mmHg		20° 10^{-5} mmHg		20° O_2; 150 mmHg	
		shape of line	He_1, oersted	shape of line	He_2, oersted	shape of line	He_3, oersted
RMT 2.2×10^4 Mrad	7.5	mixed	3	mixed	6	mixed	12
RTMP THT = 270°	7.5	mixed	6	mixed	9	mixed	12
THT = 420°	6.2	mixed	9	mixed	13	Lorentz	
THT = 550°	5.0	mixed	10	Lorentz		Lorentz	
THT = 720°	0.5	Lorentz		Lorentz		Lorentz	

separate spin packets, as shown in Figs. 9*a* and 9*b*. However, the individual spin packets are not the unresolved components of a hyperfine structure, and do not arise from the anisotropy of the *g*-factor, since the spectrum changes to a single line of Lorentz form and ΔH_{max} = 0.5 oersted when the initial products of radiation-modified polyethylene and also the products of subsequent heat treatment at 270° and 350° are subjected to prolonged vacuum treatment (up to many tens of hours) at 10^{-6} mmHg (see Figs. 8*b* and 9*c*). Thus, in the RTM products of polyethylene prepared at temperatures below 720° the commonly observed dependence of line-width upon THT is misleading and is due to the presence of a paramagnetic gas — oxygen — whose complete removal requires several days' vacuum treatment [15,16]. This effect is completely reversible and occurs without affecting the total concentration of paramagnetic centres. The Lorentz shape and the 0.5 oersted width of the line suggest considerable delocalisation of the paramagnetic centres. The reversible oxygen effect is easily explained by assuming the presence of separate delocalisation regions for paramagnetic centres. Molecular oxygen creates localised magnetic fields which are randomly distributed with respect to these regions. This must lead to a Gaussian distribution of very narrow lines, i.e. to a Gaussian shape for their envelope, if exchange interaction between the isolated delocalisation regions is absent. It has been shown [17,18] that in the presence of exchange the line adopts the Lorentz form in the centre, and the abscissa (*He*) of the point of transition from the Lorentz to the Gaussian form gives directly the frequency of the exchange interaction (see Fig. 10). Using the products of radiation-induced and radiation-thermal modification of polyethylene, we have analysed the shape of the line obtained both in the presence of oxygen at 150 mmHg pressure and after incomplete removal of the oxygen. In Fig. 10 the linear variation of $\log(y/I')$ with y^2 denotes a Gaussian shape, that between $\sqrt{y/I'}$ and y^2 denotes a Lorentz shape [18]. The results of the analysis are given in Table 3.

It is obvious from Table 3 that a line of mixed form is characteristic of the products obtained at temperatures below 550°: Lorentz in the middle and Gaussian at the tails. This means that in the presence of oxygen the system shows a characteristic exchange interaction between delocalisation regions. Deliberate addition of oxygen raises the frequency of the interaction. Inspection of Table 3 also shows that the exchange interaction increases as the measurement temperature is raised. It increases also on going from the deeply irradiated products to the products of subsequent heat treatment and on increasing the THT temperature, which determines the gradual loss of saturation of the ESR line with intensification of the RTM treatment. These results indicate a growth of the delocalisation regions. In the products of the modification of polyethylene discussed here these regions are thought to correspond to structural units with favourable polyconjugation, which grow at higher THT at the expense of the intervening, less structurally developed, layers. Since in the absence of oxygen all the products of RTM of polyethylene prepared below 750°, including the original specimens which have only been irradiated to an absorption of 2.2×10^4 Mrad, are characterised by a line of equal width (0.5 oersted) and shape (Lorentz), we may conclude that the structure of the polyconjugation regions themselves is not appreciably affected by the modification conditions. The narrow line, the independence of the line-width of measurement temperature, and the presence of line saturation in the low-temperature products all point to weak spin–orbital interaction in the system, i.e. to a low symmetry of the regions of favourable polyconjugation.

Infrared spectroscopic studies have yielded more concrete information on the nature of these regions, and have reliably demonstrated the presence of polyconjugated structures of a cyclic type in the products of RTMP. [19] The ESR and infrared data, when taken together, justify the conclusion that the polyconjugated formations detected by the ESR method correspond to these cyclic structures. As was said above, the line of width 7.5 oersted in the presence of oxygen begins to be registered by the ESR method at doses of the order of 6×10^3 Mrad. It follows that the cyclic polyconjugated structures characteristic of the products of RTMP are formed at the first stage in the modification of polyethylene, i.e. during irradiation, if the dose is high enough.

As regards the products prepared at THT > 750°, we saw in Fig. 8 that their line-width increases sharply with THT. Furthermore, the line-width in these products increases also with measurement temperature. It follows that the width of the line in these materials is determined by the spin–lattice interaction. It has been found that, in contrast to the products prepared at lower temperatures, increased duration of heat treatment transforms the line from the symmetrical Lorentz shape to an asymmetric shape, and considerably increases its width [20]. All these results point to a change in the structure of the polyconjugation regions at temperatures above 750°, in the sense of increased symmetry. Special experiments have shown that the symmetry of the polyconjugation regions increases not only with increase of the temperature of heat treatment, but also with increase of the time of heat treatment.

Thus, the structure of the RTMP products as established by the ESR method provides a complete explanation of the effects of temperature and frequency upon conductivity, listed above. Indeed, some results obtained from ESR spectra show that the polyconjugation regions are separated by narrow, structurally less perfect interlayers. These interlayers can be identified with the potential barriers opposing the drift of current carriers, whose height determines the activation energy of conduction in a d.c. field. The conductivity of the polyconjugation regions themselves is measured at high frequencies, in the region of the plateau. As shown by ESR measurements, the polyconjugation regions grow with increase of THT at the expense of the interlayers, and this leads to a decrease in the activation energy for conduction, an increase in conductivity, and a decrease in thermo-e.m.f. At the same time, the ESR data show that the structure of the polyconjugation regions themselves is practically unaffected by THT up to 750°, but begins to change appreciably with THT at higher temperatures. This is in keeping with the fact, mentioned above, that the a.c. conductivity is barely affected by changes of THT in the region between 350° and 700°.

The variation with THT of the pre-exponential term, which (as we shall show) characterises the conductivity of these regions, also suggests that changes of this type are occurring in the polyconjugation regions.

Fig. 7 shows that below 600–700° the pre-exponential term is an insensitive function of the THT, but it begins to increase sharply with THT at higher temperatures.

We have already pointed out that addition of oxygen to RTMP specimens brings about, on the one hand, a decrease in the activation energy for conduction, and, on the other hand, an intensification of the exchange interaction between polyconjugation regions. In both cases, the observed interaction occurs between the oxygen and the interlayers, and assists the transfer of electrons between regions. In accordance with this interpretation, the high-frequency conductivity in the region of the plateau should be unaffected by the presence of oxygen: this is confirmed by the experimental results (Fig. 5).

V. INFLUENCE OF IMPURITIES ON THE ELECTRICAL PROPERTIES

The effect of adsorbed oxygen on the behaviour of RTMP products suggested that a study of the interaction of these materials with iodine would be of interest, since it could be expected to produce more clear-cut effects.

It was indeed found [21,22] that the adsorption of iodine from the gas phase has a profound effect on the electrical properties of RTMP products, raising the conductivity by several orders of magnitude and at the same time lowering the activation energy, the conductivity remaining p-type for iodination temperatures up to 200°. Isotherms plotted between 100° and 200° showed that the adsorption decreases with increase of the measurement temperature, has all the characteristics of physical adsorption, and increases with increase of the temperature of heat treatment of the specimens. The degree of saturation adsorption, which obtains at p_{I_2} of 19 and 22 mmHg for THT of 420° and 720° respectively, is quite considerable, reaching values of ~ 0.2 and ~ 0.4 g of I_2 per g RTMP at an adsorption temperature of 100°. However, changes in σ and ΔE can be detected at the very much lower extents of iodine adsorption corresponding to 20–25° (i.e. at $p \simeq 1$ mmHg). This has enabled the effect of iodine to be investigated quantitatively by comparing the iodine adsorption kinetics with the kinetics of the change in electrical characteristics. The experiments were made in the presence of air rather than in a vacuum in order to decrease the rate of adsorption of iodine.

The kinetic curves obtained for a specimen subjected to a THT of 420° are reproduced in Fig. 11. It can be seen that σ increases by 6 orders of magnitude. The curve has a number of notable features: a threshold preceding the increase of σ, the narrow range over which σ increases to a maximum value, and the constancy of this maximum despite the steadily increasing extent of iodine adsorption. Fig. 12 shows the variation of σ with the extent of iodine adsorption for specimens subjected to a THT between 420°

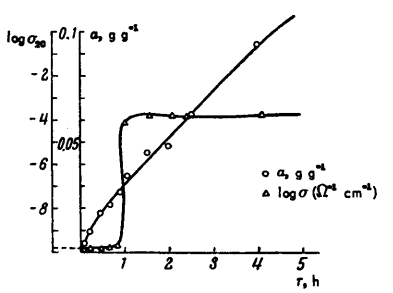


Fig. 11. Comparison of iodine adsorption kinetics and kinetics of the change of electrical conductivity for a specimen with THT = 420°.

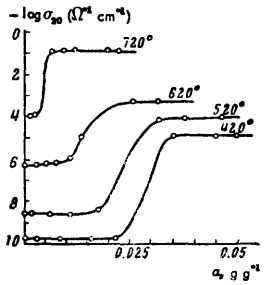


Fig. 12. Variation of σ_{20} with amount of iodine adsorbed.

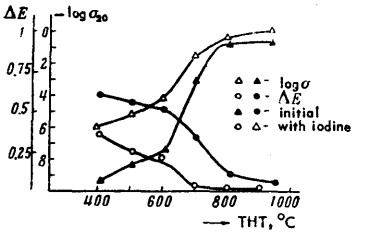


Fig. 13. Effect of THT on σ_{20} and ΔE in the presence and in the absence of iodine.

and 720°: it is evident that the amount of adsorbed iodine needed to produce a sharp change in the values of σ decreases with increase of THT, whilst the magnitude of the effect also decreases. The activation energy for conduction also changes sharply at a well defined degree of iodine adsorption: as might have been expected, the activation energy drops. Fig. 13 gives values of σ_{20} and ΔE for different THT in the absence and in the presence of iodine.

These results are in complete agreement with the ideas on the structure of RTMP products derived from ESR studies, which were discussed in the previous Section. Thus, the fact that the amount of iodine necessary to shift σ is smaller, the higher the THT, shows that iodine adsorption on the intermediate layers plays the effective role. It assists the motion of current carriers, and thus raises σ and lowers ΔE. Iodine adsorption in this case affects the potential barriers, but not the structure of the polyconjugation regions themselves, as shown by the constancy of the conductivity type. It has also been pointed out that the ESR spectra remain unchanged over the whole range of adsorption for a THT of 420°. When the polyconjugation regions become very extensive, as in the case of a THT of 720°, the ESR spectra begin to show evidence of the formation of charge-transfer complexes. This interpretation of the observed effects is also confirmed by the frequency dependence of the conductivity in the presence of adsorbed iodine. As was to be expected from the fact that potential barriers are removed, no dispersion of σ is observed in this case.

VI. CONDUCTION MECHANISM

We have shown above that the conductivity observed in the products of RTM of polyethylene is electronic and is determined by the concentration and mobility of free current carriers:

$$\sigma = e(n\mu_n + p\mu_p),$$

where e is the electronic charge, n and p are the concentrations of electrons and positive holes, and μ_n and μ_p are their respective mobilities.

In the majority of cases we shall ignore the contribution of electrons to the conductivity, since the materials of interest are p-type semiconductors, and we shall use the expression

$$\sigma = ep\mu^*, \qquad (1)$$

where μ^* is the hole mobility.

It has been shown that the conductivity in the temperature range from -25° to 150° is an exponential function of the reciprocal of temperature:

$$\sigma = \sigma_0 \exp(-\Delta E/kT). \qquad (2)$$

The mechanism of electrical conductivity is determined, essentially, by whether the activation energy generates charge carriers or whether it activates mobility of the carriers in the material. Measurement of thermo-e.m.f. is a convenient method for distinguishing between the generation and the carrier transport mechanisms in organic semiconductors. For semiconductors with carriers of a single type the thermo-e.m.f. is given by the expression

$$\alpha = \frac{k}{e}\left[A + \ln\frac{2(2\pi m^* kT)^{3/2}}{h^3 P}\right],$$

where k is Boltzmann's constant, m^* is the effective mass of the carriers, h is Planck's constant, and A is a constant whose value varies from 0.5 to 4 according to the scattering mechanism. This expression can be converted to the form

$$\alpha = B + C\ln T - D\ln p,$$

where B, C, and D are temperature-independent to a first approximation.

As was recently pointed out[23,24], the temperature variation of the concentration of current carriers for organic semiconductors can be derived from measurements of the thermo-e.m.f. as a function of temperature. Thus, if p = const, α is a very insensitive function of temperature ($\alpha \propto \ln T$), and any increase of thermo-e.m.f. may be masked by the normal experimental error over small temperature intervals. If p is an exponential function of $1/T$, we obtain a steeper variation of α with T, easily detected experimentally, namely $\alpha \propto 1/T$. Since α is independent of temperature in every sample of RTMP, we conclude that over the temperature range of the experiments

$$p = \text{const and } \mu^* = \mu\exp(-\Delta E/kT).$$

The physical significance of this expression stems from the detailed study of the structure of RTMP, based mainly on ESR spectra, which has shown that materials prepared at THT > 420° are characterised by regions with a single type of well-developed structure in which polyconjugation is prevalent, separated by narrow regions with a less well-developed structure which can be associated with the potential barriers opposing the drift of carriers.

The conductivity of the regions of polyconjugation in RTMP can be estimated from measurements at various frequencies. The observed dispersion of conductivity with frequency can be ascribed to microheterogeneity in the

specimens. The Maxwell–Wagner double-layer condenser is a classical prototype of the processes occurring in this system. Its constants C_c, R_c, C_b, and R_b are determined by the characteristics of the regions containing conjugated bonds (dielectric constant ϵ_c and resistivity ρ_c) and by those of the barriers (ϵ_b and ρ_b). If x is the ratio of barrier thickness to grain thickness and $x \ll 1$, $\epsilon_c = \epsilon_b$, and $\rho_c \ll \rho_b$ — conditions which the above arguments show to be applicable to RTMP specimens — it is possible to derive[25,26] the following limiting values for the characteristics ρ_{sp} and ϵ_{sp} of the specimen:

$$\rho_{sp}^0 = \rho_c + x\rho_b, \quad \varepsilon_{sp}^0 = \varepsilon_c \frac{\rho_c^2 + x\rho_b^2}{(\rho_c + x\rho_b)^2}, \tag{3a}$$

$$\rho_{sp}^\infty = \rho_c, \qquad \varepsilon_{sp}^\infty = \varepsilon_c, \tag{3b}$$

where the superscripts 0 and ∞ refer to zero frequency and to the high frequencies at which ρ_{sp} and ϵ_{sp} become independent of frequency. Thus, in the high-frequency region we measure the characteristics of the regions of polyconjugation (Figs. 4 and 5). It is evident from Fig. 4 that the lower the THT of the specimen, the higher is the frequency at which the conductivity plateau is reached. This is due to the increase in size of the polyconjugation regions, and to the decrease in barrier height, which occur as the THT is raised. For high THT, when $\Delta E \to 0$, the barriers become vanishingly small and no dispersion of conductivity with frequency can be detected. We may conclude that, when the THT is raised, the conductivity $\sigma_c = \sigma_f$ of the regions with polyconjugated bonds does not differ very much from the observed d.c. conductivity σ, and that whilst $\sigma_{20°}$ covers a range of some 10 orders of magnitude for different specimens, σ_f for the same specimens varies only by ~ 2 orders (Fig. 4). Studies of the temperature dependence of the plateau conductivity σ_f show an insignificant variation as compared with that of σ (Fig. 5). Therefore, in keeping with what has already been said, the activation energy for conduction in a d.c. field can be ascribed to the potential barriers. The small activation energy for conduction ΔE_f in the polyconjugation regions is associated either with the generation of current carriers or with the motion of the carriers within these regions. No data on which to base a choice between these two processes are at present available.

It follows from our discussion that

$$\sigma_f = \sigma_c = ep\mu_c, \tag{4}$$

where μ_c is the carrier mobility in the polyconjugation regions.

The barrier mechanism of conduction is applicable to the model for the structure of the material which we have been considering[27]. To obtain an expression for the macroscopic conductivity, we ignore the resistance of the polyconjugation regions and we express the current as a function of the applied voltage across the barriers[27]:

$$j = \frac{Mp}{4}[\exp(-e\psi/kT)]\,[\exp(e\Delta V_b/kT) - 1], \tag{5}$$

where j is the current density, p is the average concentration of intrinsic carriers (holes) in the polyconjugation regions, ψ is the height of the potential barrier, ΔV_b is the drop in potential across one barrier, and M is a parameter which does not depend on ψ but is a function of the specific nature of the barrier. For a barrier of 5–20 Å thickness, such as is likely to be found in our system, $M = ev_T$, where v_T is the mean thermal velocity of holes. Ohm's law is obeyed up to ~ 10^3 V cm^{-1} in the products of RTMP (Fig. 2). This suggests that the potential drop at each barrier, ΔV_b, is much less than kT/e. We can therefore re write Eqn. (5) in the form

$$j = \frac{v_T p e^2 \Delta V_b}{4kT} \exp(-e\psi/kT). \tag{6}$$

Since we are dealing with N polyconjugation regions connected in series, we can evaluate ΔV_b as

$$\Delta V_b = \frac{V}{N} = \frac{V}{nl} = \frac{\varepsilon}{n}, \tag{7}$$

where V is the voltage applied to the specimen, ϵ is the field strength, l is the length of the specimen, and n is the number of polyconjugation regions per unit length. For $\epsilon > (2.5–5) \times 10^3$ V cm^{-1} the current–voltage relationship begins to depart from Ohm's law. From this figure we can make an approximate estimate of the size of the polyconjugation regions. Since the precision of the measurements is ~ 5%, deviations from Ohm's law will be detectable at $e\Delta V_b = kT/10$. (This corresponds to 2.5×10^{-3} eV at room temperature.) Hence, from formula (6), $n \simeq (1–2) \times 10^6$ cm^{-1}. Ignoring the linear dimensions of the barriers in comparison to those of the polyconjugation regions, we estimate the size of the latter as $L \simeq$ (50–100) Å.

The macroscopic conductivity is given by the expression

$$\sigma = j/\varepsilon,$$

which when combined with Eqns. (6) and (7) gives

$$\sigma = \frac{v_T p e^4}{4kTn} \exp(-e\psi/kT) = ep\mu \exp(-e\psi/kT), \tag{8}$$

where

$$\mu = \frac{v_T e}{4nkT}.$$

The term $\exp(-e\psi/kT)$ is characteristic of the barriers. Eqn. (8) can be written in two forms:

$$\sigma = ep\mu^* \quad \mu^* = \exp(-e\psi/kT), \tag{9a}$$

$$\sigma = ep^*\mu \quad p^* = p\exp(-e\psi/kT). \tag{9b}$$

The macroscopic value of the Hall coefficient, R_H, has been found to give the value of p in systems of this type. This is because the polyconjugation regions have a much lower resistance than the barriers[27], i.e. $R_H = \frac{3}{8}\frac{\pi}{ep}$, and the Hall mobility is given by

$$\mu_H = R_H\sigma = \frac{3}{8}\pi\mu^*.$$

Therefore, the Hall mobility gives a direct measure of μ^* and includes the barrier effects.

The thermo-e.m.f. in systems of this type is also determined by the more extensive system, i.e. by the polyconjugation regions, if the temperature gradient across the barriers is insignificant[4]. This measurement therefore gives the carrier concentration p in the polyconjugation regions. It follows that the mobility derived from measurements of conductivity and thermo-e.m.f. is also equal to μ^*, and that formula (9a) is applicable. Since the hole concentration as measured from the conductivity at high frequencies and from the thermo-e.m.f. varies only slightly, we may suggest that carriers are generated by the impurity mechanism.

On comparing the equations which describe the experimentally observed relations (2) and (9a) with those deduced from the barrier mechanism, we obtain

$$\Delta E = e\psi, \quad \mu = \frac{v_T e}{4nkT}, \quad \sigma_0 = \frac{v_T e^2 p}{4nkT}. \tag{10}$$

The expressions for σ and μ^* enable μ^* and p to be calculated for RTMP specimens of different THT. In semiconductors with a non-degenerate system of carriers

$$\frac{m^*v^2}{2} = \frac{3}{2}kT. \quad (11)$$

The effective mass m^* is not known, but we can assume that in organic semiconductors the effective mass is greater than the free electron mass m, since many experimental and calculated results suggest that the bands are narrow. Table 4 lists the values of μ^* and p calculated by formulae (8) and (11) from the experimental values of σ_{20° and ΔE, assuming m^* to be m and $10m$ and making use of the size of the polyconjugation regions calculated above.

Let us consider now the expression for μ in greater detail. From (10) and (11), we have

$$\mu = \frac{3}{4}\frac{e}{m^*}\frac{L}{v_T}. \quad (12)$$

On comparing this with the expression for the mobility in the polyconjugation regions,

$$\mu_c = \frac{e}{m^*}\frac{d}{v_T} = \frac{e}{m^*}\tau, \quad (13)$$

where d is the carrier mean free path, we conclude that σ is directly determined by the conductivity of the polyconjugation regions through (12), (13), and (8):

$$\sigma = \mu_c p \frac{3}{4}\frac{L}{d}\exp(-\Delta E/kT) = \frac{3}{4}\frac{L}{d}\sigma_c\exp(-\Delta E/kT). \quad (14)$$

Thus we find that the d.c. conductivity in systems of this type is clearly determined by the conductivity of the polyconjugation regions (σ_c) and by the interlayers of structurally less perfect material (ΔE).

We showed in the experimental section that the relationship

$$\sigma_0 \simeq \sigma_f = \sigma_c \quad (15)$$

holds for specimens of RTM polyethylene. Hence, $\frac{3}{4}\frac{L}{d} \simeq 1$, the mean free path d is approximately equal to the dimensions (L) of the polyconjugation regions, and Eqn. (14) takes the following form for RTM polyethylene specimens:

$$\sigma \simeq \sigma_c\exp(-\Delta E/kT).$$

In general, σ_0 can be greater or smaller than σ_c according to the value of the ratio L/d, and this ratio can be evaluated from measurements in a d.c. and an a.c. field.

TABLE 4.

THT, °C	$D = 2.4\times10^4$ Mrad, $L = 100$ Å			
	$m^* = m$		$m^* = 10m$	
	μ^*, cm² V⁻¹ s⁻¹	p, cm⁻³	μ^*, cm² V⁻¹ s⁻¹	p, cm⁻³
420	5×10^{-7}	1.3×10^{18}	1.5×10^{-5}	4.2×10^{18}
520	6.3×10^{-4}	2×10^{18}	1.8×10^{-3}	6.6×10^{18}
620	2×10^{-3}	2.3×10^{18}	6×10^{-4}	7.6×10^{18}
725	2×10^{-1}	2×10^{16}	7×10^{-3}	6×10^{16}
825	20	2×10^{17}	6	6×10^{17}
930	115	3.5×10^{18}	35	1.2×10^{19}
	$D = 2.4\times10^4$ Mrad, $L = 50$ Å			
420	2.5×10^{-5}	2.6×10^{18}	7.5×10^{-4}	8.4×10^{18}
520	3.1×10^{-3}	4×10^{18}	9×10^{-4}	1.3×10^{14}
620	1.0×10^{-2}	4.6×10^{18}	3×10^{-1}	1.5×10^{14}
725	1×10^{-1}	4×10^{16}	3.5×10^{-2}	1.2×10^{16}
825	10	4×10^{17}	3	1.2×10^{16}
930	57	7×10^{18}	17	2.4×10^{19}

The regions of bond polyconjugation are characterised by high mobility (~ 17–115 cm² V⁻¹ s⁻¹) and conductivity (~ 10^{-4}–10^{-2} Ω⁻¹ cm⁻¹), but the effective mobility μ^* and the conductivity σ_{20° of RTMP specimens are very much lower, due to the presence of potential barriers.

This discussion is only approximate, because it is confined to carriers of a single kind. However, we have observed[7] an increase in positive thermo-e.m.f. in the presence of oxygen which can be explained by postulating an electronic contribution to the conductivity in addition to the hole conductivity.

VII. NATURE OF THE PARAMAGNETISM

A limited understanding of the nature of the paramagnetism of the RTM products of polyethylene was derived from studies of the reversible oxygen effect and from comparisons of the paramagnetic and electrical properties of given specimens. As stated above, the reversible oxygen effect in products prepared at temperatures below 500° consists in the generation of localised fields and in the intensification of exchange interactions between delocalisation regions of paramagnetic centres. The latter effect indicates that overlap of electron orbitals is taking place between an oxygen molecule and the paramagnetic centres, but that the overlap is not affecting the paramagnetic centre concentration. With products obtained at temperatures in excess of 500° the delocalisation regions grow at the expense of the intervening layers to such an extent that the steric conditions leading to a more intimate overlap of the orbitals are satisfied. In these products the concentration of paramagnetic centres varies on admission of oxygen. A comparison of the reversible oxygen effect has been made on RTM products of polyethylene which had been subjected to vacuum pyrolysis with and without a preliminary oxidation: such a comparison is essential to an understanding of the role of the oxygen present in the structure of the pyrolysis products.

If the samples for irradiation are pre-oxidised, the concentration of unpaired spins in the products prepared at temperatures between 550° and 750° increases reversibly upon admission of oxygen. Measurements on a number of materials which had been heat-treated for various times at ~ 700° showed that the adsorption is physical in nature since it has a heat of 2 kcal mole⁻¹. It was shown that the adsorption of 1 molecule of oxygen on pre-oxidised products heated at moderate temperatures causes the loss of 2 unpaired spins. This ratio justifies the conclusion that the paramagnetism of RTM of polyethylene is due to the presence of isolated paramagnetic centres, and not to a weak interaction between strongly conjugated systems [28]. A further conclusion from the observed relationship is that the physical adsorption of oxygen on pre-oxidised products involves reversible pairing of two unpaired electrons from the specimen with two unpaired electrons from an oxygen molecule without disruption of the O=O bonds.

If the pre-oxidation stage is omitted in the preparation of these materials, the paramagnetic centre concentration in the products treated at moderately high temperatures does not increase, but rather decreases reversibly upon admission of oxygen. A similar effect is observed for many organic compounds with well developed polyconjugation systems. The effect is universally ascribed to the formation of charge-transfer surface complexes of the donor–acceptor type [13]. A comparison of the number of

adsorbed oxygen molecules with the number of the resulting paramagnetic centres has been made for RTM products prepared at 700°. The adsorption is again physical in nature, since it increases on lowering the temperature, the heat of adsorption being 2.5 kcal mole^{-1}. It has been shown that each oxygen molecule adsorbed causes the appearance of 1 paramagnetic centre. From this comparison of the effect of oxygen on the concentration of paramagnetic centres in RTM products of polyethylene with and without a preliminary oxidation treatment, we may conclude that oxygen-containing groups hinder the formation of charge-transfer complexes. This is probably because they compete with molecular oxygen, "drawing" the electron cloud around themselves. It has been found that the adsorption of 1 oxygen molecule induces 1 paramagnetic centre even in products prepared above 750°, whether or not the products are pre-oxidised before vacuum pyrolysis. This effect is probably associated with practically complete removal of the oxygen-containing groups from the structure of the products during high-temperature pyrolysis.

Fig. 14 shows, as a function of THT, the concentration of paramagnetic centres in vacuum-treated RTMP samples and the concentration of current carriers calculated for assumed carrier effective masses (m^*) of m and $10m$ (lower and upper boundaries of the cross-hatched band respectively).

It is clear that the concentration of paramagnetic centres in materials prepared below 800° is higher than the carrier concentration by many orders of magnitude, and that the two concentrations vary with THT in different ways.

The conclusion to be drawn from this comparison is that the paramagnetic centres in materials of this type (including specimens subjected to irradiation only) cannot be identified directly with charge carriers. The centres are apparently caused by structural defects. As stated above, the analysis of the ESR spectra indicates that the unpaired electrons bound to structural defects are delocalised within the individual polyconjugation regions. It is obvious from Fig. 14 that for temperatures above 600° the concentration of defects decreases whilst the concentration of charge carriers increases steeply with THT. Furthermore, in the materials prepared at THT > 800° the concentration of paramagnetic centres begins to increase once again with increase of THT at much the same rate as the concentration of current carriers. Unlike the low-temperature and the intermediate-temperature products, freshly prepared high-temperature products show an increase in paramagnetic centre concentration with increase in measurement temperature. This result has led to the conclusion that current

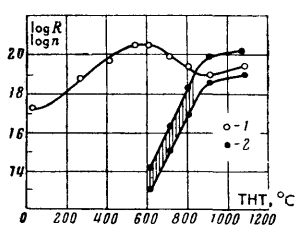


Fig. 14. Effect of THT on the concentration of paramagnetic centres (curve 1) and on the concentration of charge carriers (curves 2).

TABLE 5.

THT	μ^*, cm^2 V^{-1} s^{-1} p, cm^{-3} or g^{-1}	Electrical measurements		ESR	
		$m^* = 10m$	$m^* = m$	$m^* = 10m$	$m^* = m$
930	μ^*	17	115	13	130
	p	2.4×10^{19}	3.5×10^{18}	7×10^{18}	
1100	μ^*	17	115	13	130
	p	3.6×10^{19}	5.2×10^{18}	1.5×10^{19}	

carriers are responsible for the ESR signal in this particular case. When surface oxides are formed on these products, the concentration of paramagnetic centres becomes independent of measurement temperature. The relaxation time τ_R of the carriers[30] has been obtained from the parameters of the ESR spectra — line width (Fig. 8) and the g-factor (2.0027) — for materials prepared at 930° by means of the formula

$$T_1 = \left(\frac{3\times10^{-8}}{\Delta H_{max}}\right) = \frac{1}{30}\,\frac{\tau}{(g-g_{free})^2},$$

given by Elliott[29]. As in the case of the electrical measurements, the numerical values of mobility were obtained from formula (13) by assuming effective masses of $1m$ and $10m$.

In this way, the mobility and carrier concentration have been calculated by independent methods: it is evident from the values obtained, which are set out in Table 5, that the agreement between the two sets of results is satisfactory. The measured conductivity of a specimen prepared at THT = = 930° is 56 Ω^{-1} cm^{-1}. Assuming that the density of the products is 1.5 g cm^{-3}, we conclude that $m^* \simeq 4m$, since the mobility is 50 cm^2 V^{-1} s^{-1} at a carrier concentration of 7×10^{18} g^{-1} (as determined by the ESR method).

These results prove that the application of the ESR method to studies of polymeric materials having semiconducting properties can assist in the identification of some of the features of the conduction mechanism in these materials as well as giving information on their structural characteristics.

In conclusion, we can say that the radiation-thermal modification of linear polymers, which we have studied in the particular case of polyethylene, offers the possibility of preparing organic semiconductors showing a wide range of properties.

1. A.N. Terenin, Uspekhi Khim., 24, 121 (1955).
2. "Organic Semiconductors. Proceedings of an Inter-Industry Conference, New York, 1962" (Translated into Russian), Izd. "Mir", Moscow, 1965.
3. L.S. Stil'bans, L.D. Rozenshtein, et al., "Organicheskie Poluprovodniki" (Organic Semiconductors), Izd. Akad. Nauk SSSR, Moscow, 1963.
4. F. Winslow, W. Baker, and W. Jager, J. Amer. Chem. Soc., 77, 4751 (1955).
5. A.V. Topchiev, M.A. Geiderikh, V.A. Kargin, et al., Dokl. Akad. Nauk SSSR, 128, 312 (1959).
6. N.A. Bakh, V.D. Bityukov, A.V. Vannikov, and A.D. Grishina, Dokl. Akad. Nauk SSSR, 144, 135 (1962).
7. A.V. Vannikov and N.A. Bakh, Elektrokhimiya, 1, No. 5 (1965).
8. A.V. Vannikov, V.D. Bityukov, and N.A. Bakh, Symposium "Khimicheskie Svoistva i Modifikatsiya Polimerov" (Chemical Properties and Modification of Polymers), Izd. "Nauka", Moscow, 1964, p. 41.

9. L. Boguslavsky and A.V. Vannikov, J. Electrochem. Soc., 111, 755 (1964).
10. A.V. Vannikov, G.N. Demidova, L.D. Rozenshtein, and N.A. Bakh, Dokl. Akad. Nauk SSSR, 160, 635 (1965).
11. A.G. Koritskii, Yu.N. Molin, V.N. Shamshev, N.Ya. Buben, and V.V. Voevodskii, Vysokomol. Soed., 1, 118a (1959).
12. S.-I. Ohnishi, S.-I. Sugumoto, and I. Nitta, J. Polymer Sci., p.A. 1, 605 (1963).
13. A.D. Grishina and N.A. Bakh, Vysokomol. Soed., 7, 1692 (1965).
14. A.D. Grishina, V.A. Larin, and N.A. Bakh, "Trudy Simpoziuma po Radiatsionnoi Khimii Polimerov" (Proceedings of the Symposium on the Radiation Chemistry of Polymers), Moscow, 1964.
15. A.D. Grishina and N.A. Bakh, "Trudy Vsesoyuznogo Soveshchaniya po Izucheniyu Tverdogo Tela Metodami Magnitnogo Rezonansa" (Proceedings of the All-Union Conference on the Study of Solids by Magnetic Resonance Methods), Krasnoyarsk, 1964.
16. A.D. Grishina and N.A. Bakh, Zhur. Strukt. Khim., 6, 194 (1965).
17. P.W. Anderson and P.R. Weiss, Rev. Mod. Phys., 25, 269 (1953).
18. N.N. Tikhomirova and V.V. Voevodskii, Optika i Spektrosk., 7, 829 (1959).
19. Z.A. Markova, B.G. Ershov, and N.A. Bakh, Vysokomol. Soed., 6, 131 (1964).
20. A.D. Grishina and N.A. Bakh, Zhur. Strukt. Khim., 6, 204 (1965).
21. A.V. Vannikov and N.A. Bakh, Dokl. Akad. Nauk SSSR, 152, 905 (1963).
22. N.A. Bakh, A.V. Vannikov, A.D. Grishina, Z.A. Markova, and S.V. Nizhnii, "Trudy Simpoziuma po Radiatsionnoi Khimii Polimerov" (Proceedings of the Symposium on the Radiation Chemistry of Polymers), Moscow, 1964.
23. C.G.B. Garrett, Radiation Res. Suppl., 2, 340 (1960).
24. R.M. Voitenko and E.M. Raskina, Dokl. Akad. Nauk SSSR, 136, 1137 (1961).
25. C. Koops, Phys. Rev., 83, 121 (1951).
26. P. Miles, W. Westphal, and A. von Hippel, Rev. Mod. Phys., 29, 279 (1957).
27. R. Petritz, Phys. Rev., 104, 1508 (1956).
28. L.A. Blyumenfel'd, V.V. Voevodskii, and A.G. Semenov, "Primenenie Elektronnogo Paramagnitnogo Rezonansa v Khimii" (Applications of Electron Spin Resonance in Chemistry), Novosibirsk, 1962, p.218.
29. I.R. Elliott, Phys. Rev., 96, 266 (1954).
30. A.D. Grishina and A.V. Vannikov, Dokl. Akad. Nauk SSSR, 156, 647 (1964).

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EFFECT OF CHEMISORBED GASES ON THE WORK FUNCTION OF METALS

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Most of the work on the mechanism of the adsorption and chemisorption of gases on metals has been concerned with the kinetics of these processes and with the relevant heats of adsorption. Yet, attempts were made as long ago as in the 1930's to establish a connection between the rate of interaction of gases with metals and the change in work function of the metals.

Rideal and his coworkers [1] studied the relationship between the activation energy and the work function. Langmuir [2], de Boer [3], Lukirskii [4], and others, measured the change in contact potential difference (c.p.d.) resulting from the adsorption of alkali metal atoms on tungsten, and from the adsorption of oxygen and hydrogen on alkali metals. However, the literature of that period contains various contradictory results as well as some very valuable papers: this state of affairs, which was due to the inadequacy of existing measurement techniques, was responsible for the loss of interest in this problem. In recent years, modern theories of gas–metal interactions and the development of high-vacuum and electronic measurement techniques gave new impetus to studies of the mechanism of the adsorption of gases on metals and of their influence on the work function. Recent investigations include the effect of the adsorption of hydrogen, oxygen, carbon monoxide, the noble gases, etc., on the work function of metals, and some attempts at establishing the relation between the changes in work function and in heat of adsorption under conditions of increasing surface coverage [5,6].

The results of work function measurements as a function of gas adsorption were used by several workers to calculate heats of adsorption. Eley [7] suggested the use of a semi-empirical formula, based on Pauling's equation for the energy of a covalent bond:

$$-\Delta H_0 = H_c + 23.06\,(x_m - x_a)^2, \qquad (1)$$

where H_C is the initial energy of the covalent bond, and $(x_m - x_a)$ is the electronegativity difference between the adsorbent and the adsorbate.

Calculations of the heat of adsorption of hydrogen chemisorbed on tungsten, using this equation, agree satisfactorily with experimental data. However, the adsorption of oxygen, nitrogen, and also some organic molecules gave appreciable discrepancies between calculated and experimental values. Eley's calculation presupposes a linear change of contact p.d. with surface coverage, which is not always borne out by the experimental results.

The contact p.d. method has been used also to examine the mechanism of catalytic and electrochemical processes.

Work function values are of major significance [8,9] in problems involving the Volta potential, which, according to the ideas developed by Frumkin, determines the relation between the points of zero charge of metals and their work functions.

The contact potential difference in the chemisorption of gases on metals depends on the nature of both the adsorbent and the adsorbate [5,6,10]. In most cases, chemisorption of gases produces a covalent bond of partially ionic character. Under these conditions, the appearance of a surface potential is associated with the transfer of an electron from the adsorbent to the adsorbate or *vice versa*. These processes lead to an increase or a decrease in the work function respectively. According to the ideas of a number of workers [5,6,10], the sign of the surface potential of the metal, $\Delta\varphi$, is determined by the difference between the work function (φ) and the electronegativity of the adsorbate (ψ):

$$\Delta\varphi = \varphi - \psi. \qquad (2)$$