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Abstract

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ON THE RECTIFYING EFFECT IN ORGANIC SEMICONDUCTORS

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In previous works it was established that products of radiation-thermal modification (r.t.m.) of polyethylene possess a definite complex of electrophysical properties ([1,2]). It was also shown that the introduction of iodine into these products substantially affects these properties. In particular, under certain conditions of iodine treatment it was possible to obtain samples which, in air at room temperature, exhibit *n*-type conductivity, in contrast to the initial samples with *p*-type conductivity. Further improvement of the electrophysical properties of r.t.m. products of polyethylene is connected with a detailed study of the conduction mechanism, in particular the mechanism of mobility of free charge carriers. It was shown earlier that in materials with *p*-type conductivity the exponential increase of conductivity with the measurement temperature is apparently connected with the activation motion of charge carriers through the heterogeneous structure of r.t.m. polyethylene. The experimental results presented in the present article confirm this conclusion.

Table 1

Sample	σ^{20°, ohm$^{-1}\cdot$ cm^{-1}	ΔE, eV	σ_0, ohm$^{-1}\cdot$ cm^{-1}	σ , ohm$^{-1}\cdot$ cm^{-1}
Initial	$1\cdot10^{-9}$	0.32	$3\cdot10^{-4}$	$3\cdot10^{-4}$
Iodinated	$4\cdot10^{-4}$	0.01	$6\cdot10^{-4}$	$4\cdot10^{-4}$

Samples of high-pressure polyethylene were studied, irradiated on an electron accelerator up to an absorbed dose of $\sim 10^{24}$ eV/g and then pyrolyzed by the standard procedure at various temperatures of thermal treatment (t.t.). As was established earlier ([1]), the conductivity of non-iodinated samples strongly depends on frequency, reaching a constant value σ in the region of 5–12 MHz, which determines the conductivity of regions of spatial polyconjugation. The conductivity in a constant field σ depends exponentially on temperature, which is determined by the exponential dependence of the mobility of charge carriers, in turn caused by barriers between regions of polyconjugation, and by the constancy of the carrier concentration, as follows from the independence of the

Fig. 1. Static current-voltage characteristics

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thermo-e.m.f. from temperature. One may therefore write, taking into account that the carriers are holes:

$$\sigma \;\; = \sigma_0 e^{-\Delta E/kT}, \qquad \sigma \;\; = n\mu e_+, \quad \text{where } n = \text{const.}$$

$$\mu = \mu_0 e^{-\Delta E/kT}, \tag{1}$$

where μ_0 characterizes the mobility in the regions of polyconjugation.

At sufficiently high temperatures all free carriers possess sufficient energy to overcome the barriers; consequently, the mobility does not depend on the barriers, $\mu = \mu_0$, and the conductivity must approach σ , i.e.

$$\mu_0 n e_+ = \sigma_0 \simeq \sigma \;\; . \tag{2}$$

As was shown, iodine lowers the potential barriers between regions of polyconjugation. When optimal amounts of iodine are introduced into a sample,

with a t.t.o. of 440° the activation energy of conductivity, calculated from measurements in a constant field, proved to be equal to ~ 0.01 eV. It may be expected that in this case the absence of barriers will lead to the conductivity not depending on frequency and being equal to σ_{hf} for the undoped initial sample, i.e., the following equality should hold:

$$\sigma_{\text{iod}} \simeq \sigma_0 \simeq \sigma_{\text{hf}}. \tag{3}$$

The experimental results obtained for the initial and iodinated sample with a t.t.o. of 440° are given in Table 1.

Fig. 1. Static current-voltage characteristics

As is seen from the data of Table 1, in the iodinated sample there is a complete absence of dispersion of conductivity with frequency, and σ is equal to $4 \cdot 10^{-4}\ \Omega^{-1}\text{cm}^{-1}$ in measurements in a constant field and up to 25 MHz. From the data presented it follows that equality (3) is well satisfied, i.e., the model proposed earlier is fully confirmed.

From electrical measurements carried out on p-type samples, when intrinsic conductivity is realized [2], one can estimate the absolute values of mobility in the products of p.t.m. polyethylene. Provided that in n-type samples there are no barriers for the passage of charge carriers, that the component of mobility which does not depend on barriers is close in n- and p-type samples, and using the usual formulas for semiconductors, we obtain that μ_0 is of the order of $\sim$ 10—100 $cm^2/V \cdot s$, i.e., it approaches in magnitude the mobility values observed in inorganic semiconductors. At the same time, the mobility at room temperature in undoped products of p.t.m. polyethylene obtained at t.t.o. up to $\sim 700^\circ$ is low, as in most studied organic semiconductors, $\sim 10^{-3}$—10^{-5} $cm^2/V \cdot s$, due to the activation term in (1). Using samples with n- and p-conductivity, one can fabricate a p—n junction, taking into account that the mobility in iodinated and pyrolyzed samples at high t.t.o. is close to μ_0, since the barriers are small.

The possibility of obtaining a p—n junction in organic substances was reported in work [(3)]. A film of saran was irradiated with unfiltered ultraviolet light, and the local surfaces absorbed different doses.

At the boundary of differently irradiated surfaces, rectification was observed under illumination with far ultraviolet, whereas without illumination no such effect was observed. The film had a specific resistance $> 10^{11}\ \Omega \cdot cm$, and the choice between an electronic and an ionic conduction mechanism is difficult. In the work of Fialkov and Davidovich ([4]), the possibility of realizing a p–n junction in carbon-graphite materials was reported.

To obtain p–n junctions in the present work, powders of high-pressure polyethylene were pressed with a small addition of low-pressure polyethylene at a temperature of 120° and a pressure of $\sim$ 10 000 atm. Preliminary experiments showed that pressed tablets made from high-pressure polyethylene with an addition of LPP practically retain the electrophysical properties of the original powders. Layers with p- and n-type conductivity on one specimen were obtained by several methods; however, the electrical characteristics of specimens prepared by different methods were close to one another. The current through the specimen was measured as a function of forward and reverse bias. Typical static current-voltage characteristics for three specimens are given in Fig. 1. As can be seen from the figure, the maximum rectification coefficient lies in the bias range 400–600 mV and reaches a value of 10–25. The dynamic current-voltage characteristics agree well with the static ones. Rectification is observed up to several kilohertz. The small rectification coefficient is evidently connected with the fact that, in powder systems, it is difficult to obtain a rectifying contact over the entire cross section of the specimen. A possible equivalent circuit of the specimen is shown in Fig. 2.

Fig. 2. Equivalent circuit of the specimen

The resistances of the n- and p-layers, R_1 and R_2, are respectively $\sim 10^4$ and $10^2\ \Omega$. R_3 determines the resistance of the transition region between the n- and p-layers, and B is the rectifying contact. It is clear from the circuit that the total current in the circuit is determined by the relationship among R_1, R_3, and B. At $R_3 \ll R_1$, rectification will not be observed in the circuit at all, even for large rectification coefficients B. If $R_3 \sim 10^5\ \Omega$, then the rectification coefficient in the overall circuit is ~ 10. The data presented indicate the possibility of obtaining a p–n junction in organic semiconductors. Further improvement of the rectification characteristic should proceed by obtaining macroscopically homogeneous specimens.

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Note: Figure translations are in progress. See original paper for figures.