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Abstract

Full Text

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EFFECT OF IODINE ON THE ELECTRICAL PROPERTIES OF PRODUCTS OF RADIATION-THERMAL MODIFICATION OF POLYETHYLENE

(Presented by Academician A. N. Frumkin, 18 X 1962)

As was established earlier ⁽¹⁾, products of radiation-thermal modification of polyethylene possess a complex of electrophysical properties that vary regularly depending on the irradiation dose and the temperature of thermal treatment (t.t.). As the t.t. increases, the conductivity increases, the activation energy decreases, and at the same time the thermoelectric power decreases. Investigation of the structure by EPR ⁽¹⁾ and IR spectroscopy, as well as investigation of the frequency dependence of the conductivity ⁽¹⁾, led to the conclusion that these materials are characterized by the presence, already at low t.t., of well-conducting regions of spatial polyconjugation, separated by less ordered interlayers, which gradually become structured as the t.t. is raised. In all cases the sign of the thermoelectric power corresponded to *p*-type conductivity. It was also established that, under certain conditions, the presence of oxygen causes an increase in conductivity and a decrease in activation energy; the thermoelectric power in this case, however, does not decrease but increases. Such a violation of the correlation between σ_{20° , ΔE , and the thermoelectric power drew attention to the possibility of changing their relationship by means of additives. In particular, taking into account the increase in conductivity of polynuclear aromatic hydrocarbons upon adsorption of iodine known from the literature ^(2,3), it was of interest to investigate the effect of this additive on the properties of the products of radiation-thermal modification of polyethylene that are of interest to us.

The samples studied were prepared from high-pressure polyethylene as described in ⁽¹⁾; the conductivity σ and thermoelectric power α were measured relative to platinum. The dose obtained in the reactor channel was $1.5 \cdot 10^{24}$ eV/g, and the t.t. was 295, 350, 445, 520, 620, and 785°.

The first series of iodinated samples was prepared by adsorption of iodine vapor at +20° followed by holding in air. In all cases an increase in conductivity by 4-6 orders of magnitude and a decrease in activation energy were observed, whereas the thermoelectric power changed comparatively little. The new properties are

Figure 1

Figure 1: Figure 1

stable at ordinary temperature and are well reproduced from sample to sample. In comparison with noniodinated samples of the same conductivity, which correspond to higher t.t., the thermoelectric power of the iodinated materials is considerably higher. Typical characteristics illustrating these relationships are given in Table 1.

Table 1

t.t., °C	I_2	σ_{20° , $\text{ohm}^{-1}\cdot\text{cm}^{-1}$	ΔE , eV	α , $\mu\text{V}/\text{deg}$
445	No	$3 \cdot 10^{-10}$	0.63	
445	Ads. at +20°	$0.8 \cdot 10^{-3}$	0.35	+150
805	No	$0.8 \cdot 10^{-3}$	0.1	+23
620	No	$7.2 \cdot 10^{-9}$	0.55	+220
620	Ads. at +20°	$1 \cdot 10^{-3}$	0.27	+140

The thermoelectric power of noniodinated products of radiation-thermal modification of polyethylene does not depend on temperature ⁽¹⁾. From this it may be concluded that the concentration of charge carriers does not change with temperature, and the exponential increase in conductivity is determined by the temperature dependence of the mobility

carriers. The measured activation energy should naturally be ascribed to potential barriers between regions of polyconjugation. In such systems the thermoelectric e.m.f. does not depend on the potential barriers ^(4,5) and characterizes the regions of polyconjugation. The decrease in ΔE and the sharp increase in σ_{20° without a substantial change in α upon introducing iodine by the method described can be interpreted as a lowering, by iodine adsorbed at +20°, of the potential barriers for the passage of current carriers, without any substantial influence on the regions of spatial polyconjugation. This is confirmed by the weak dependence of α on temperature, shown in Fig. 1a for a specimen with a heat-treatment temperature of 620°. Thus, like oxygen, iodine adsorbed at +20° disturbs the correlation between σ , ΔE , and α that characterizes the products of radiation-thermal modification of polyethylene.

Fig. 1. Effect of iodine adsorbed at +20° on the conductivity (b) and thermoelectric e.m.f. (a) of a product of radiation-thermal modification of polyethylene (heat-treatment temperature 620°). *I*—first measurements after preparation; *II*—repeated measurements after heating to 125°. 1—measurements on cooling, 2—on heating.

Figure 2

Figure 2: Figure 2

From -80° to $+20^\circ$, $\lg \sigma$ is linearly related to $1/T$. From the slope in this region, the above activation energy was calculated. With a further rise of temperature to $+125^\circ$, the increase in conductivity slows down. Evidently, a new type of interaction of the adsorbed iodine with the substrate begins. Upon subsequent lowering of the temperature, the conductivity decreases along curve *II*, which lies below curve *I* and corresponds to a higher activation energy. In repeated measurements up to $+100^\circ$, all the values lie on curve *II*, i.e., the product of interaction with iodine formed at 125° is quite stable.

To study the properties manifested under these conditions, a series of experiments was carried out with introduction of iodine at elevated temperature. Products of radiation-thermal modification of polyethylene of different heat-treatment temperatures, together with iodine purified by double sublimation, were placed in ampoules and evacuated at -50° and 10^{-4} mm. The ampoules were then sealed and heated at 240° . The specimens obtained in this way acquired new properties. In all cases the conductivity increased substantially, but the activation energy increased as well, while the thermoelectric e.m.f. exhibited a sharp dependence on temperature,

Curve *I* in Fig. 1b represents the dependence of conductivity on temperature for the same specimen, taken immediately after its preparation. As can be seen, in the region from -80° to $+20^\circ$, $\lg \sigma$ is linearly related to $1/T$. From the slope in this region, the activation energy given above was calculated. With a further rise of temperature to $+125^\circ$, the increase in conductivity slows down. Evidently, a new type of interaction of the adsorbed iodine with the substrate begins. Upon subsequent lowering of temperature, the conductivity decreases along curve *II*, which lies below curve *I* and corresponds to a higher activation energy. In repeated measurements up to $+100^\circ$, all values lie on curve *II*, i.e., the product of interaction with iodine formed at 125° is quite stable.

Fig. 2. Effect of iodine introduced at 240° on the conductivity (1) and thermoelectric e.m.f. (2) of a product of radiation-thermal modification of polyethylene (heat-treatment temperature 445°).

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from positive (*p*-type conductivity) to negative (*n*-type conductivity). The general course of the temperature dependence of σ and α can be divided into three regions, as illustrated in Fig. 2 for a specimen with m.p.t. 445° . At low temperatures (in this case below -50°), the increase of σ corresponds to small ΔE , while α depends only weakly on temperature. Subsequently the increase of σ accelerates, and α decreases sharply, passes through zero, and then reaches a maximum negative value. At higher temperatures (in this case above $+20^\circ$),

log σ depends linearly on $1/T$ with a larger value of ΔE ; α also depends linearly on $1/T$, decreasing in absolute value. The above course of the change of σ and α with temperature is analogous to the temperature dependence of these quantities for inorganic semiconductors in the case of the transition of an impurity semiconductor into an intrinsic one with increasing temperature ⁽⁶⁾. Assuming that the latter temperature region on curve 2 of Fig. 2 corresponds to intrinsic conductivity, and adopting in this region for the thermo-e.m.f. the expression ⁽⁶⁾

$$\alpha = -\frac{k}{e} \left(\frac{c-1}{c+1} \right) \left(\frac{\Delta E}{2kT} + 2 \right),$$

where c is the ratio of the mobility of electrons and holes, we obtain from the experimental data in the linear region $c = 1.23$ and a band-gap width of 1.2 eV, i.e., a value sufficiently close to the value ΔE found from the temperature dependence of the conductivity.

Table 2

m.p.t., °C	σ_{20° , ohm ⁻¹ ·cm	σ_{20° , ohm ⁻¹ ·cm	J_2/σ_{20° , cm ⁻¹	ΔE , eV	ΔE , eV, J_2	α , $\mu\text{V}/\text{deg}$, J_2		
						α , $\mu\text{V}/\text{deg}$, initial	J_2 low t°	J_2 high t°
295	10^{-12}	$3.2 \cdot 10^{-6}$	$3.2 \cdot 10^6$	0.82	1.46			-250
350	$5 \cdot 10^{-11}$	$1 \cdot 10^{-5}$	$2 \cdot 10^5$	0.66	1.10		+400	-100
445	$3 \cdot 10^{-10}$	$2.5 \cdot 10^{-5}$	$8 \cdot 10^4$	0.63	1.07		+400	-200
520	10^{-9}	$6.2 \cdot 10^{-5}$	$6.2 \cdot 10^4$	0.60	0.80	+500	+150	-10
600	10^{-8}	$5 \cdot 10^{-5}$	$5 \cdot 10^3$	0.54	0.40	+240	+160	
785	10^{-2}	1.8	$1.8 \cdot 10^2$	0.14	0.11	+15	+10	

Table 2 gives comparative characteristics of specimens iodinated at 240° and of the initial specimens, corresponding to various m.p.t.

As can be seen, the effectiveness of the introduced iodine, expressed in the relative increase of σ , is especially significant in materials corresponding to m.p.t. < 500°, and decreases regularly as the m.p.t. increases. This confirms the validity of the assumption that iodine primarily facilitates the motion of current carriers through weakly structured interlayers. However, the substantial

increase in the activation energy indicates changes that also affect the regions of spatial polyconjugation themselves.

The results obtained are insufficient for considering the mechanism of the effect of iodine on the electrical properties of the products of r.t.m. of polyethylene, but they already show the possibility of producing organic materials with a prescribed type of conductivity.

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