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Abstract

Full Text

Physical Chemistry

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Electrical and Paramagnetic Properties of Products of Radiation-Thermal Treatment of Polyethylene

(Presented by Academician A. N. Frumkin, December 25, 1961)

The present work is devoted to the study of the gradual transition of a linear dielectric polymer into a material with properties characteristic of semiconductors under radiation and thermal action. Polyethylene was chosen as a polymer simple in structure and well studied with respect to radiation transformations. Pre-evacuated high-pressure polyethylene was irradiated in a reactor channel at a temperature of $\sim 60^\circ\text{C}$ up to an absorbed dose of $\sim 10^{24}$ eV/g. It is known that at sufficiently large irradiation doses polyethylene is cross-linked into a spatial network, with the formation of simple and conjugated double bonds and five- to eight-membered rings^(1,2). However, this still does not create a sufficiently regular structure of the material as a whole, and the conductivity in a constant field remains low. The results obtained by us show that the conductivity can be substantially increased by subsequent thermal treatment at various temperatures. Unirradiated polyethylene cannot be treated under the same conditions, since it melts at $t > 100^\circ$ and decomposes. The effectiveness of pyrolysis in vacuum of a pre-irradiated polymer is promoted by the presence in it of oxygen-containing compounds (carbonyl, alcohol, ether, and other groups), which can be produced by short-term thermal preoxidation⁽³⁾ or by irradiation in the presence of oxygen. Under these conditions pyrolysis can be carried out in vacuum up to 1000° and higher, with a yield of more than 50%.

The electrophysical properties of the products obtained were characterized by conductivity in a constant field, activation energy, thermo-e.m.f., and conductivity in an alternating field; structural features were characterized by EPR spectra. The materials were studied in the form of powders pressed between disk electrodes in a measuring cell made of Teflon, placed in a glass bulb with metal leads. The apparatus made it possible to maintain a vacuum of $\sim 10^{-5}$ mm Hg and a temperature from -180° to $+200^\circ$. For measuring large resistances, a bridge electrometric circuit with an EMU-3 amplifier or an F-57 teraohmmeter with recording on an EPP-09 was used; for small resistances, a Wheatstone bridge or a PPTV-1 potentiometer was used.

The conductivity proved to be independent of pulverization of the powder and

Figure 1

Figure 1: Figure 1

Figure 2

Figure 2: Figure 2

of the nature of the electrodes (Cu, Ni, Al). The differential thermo-e.m.f. was determined relative to copper. To measure conductivity in an alternating field, the resonance method⁽⁴⁾ was used, with inclusion of the sample in the circuit of a Q meter, applicable for conductivities from 10^{-5} to 10^{-1} in the frequency range from 100 kHz to 20 MHz.

The EPR spectra were studied on an RE-1301 radiospectrometer.

Figure 1A shows the course of the change in σ_{20° , measured in vacuum, as a function of the temperature of thermal treatment in vacuum (t.t.t.) at various absorbed doses. (For the designations, see the caption to Fig. 1.) In what follows, the samples are designated by the series number with an index corresponding to the t.t.t.

As can be seen, in all cases σ_{20° increases monotonically with increasing t. t. o., passing through the range from $\sigma \sim 10^{-16}$ in nonpyrolyzed irradiated polyethylene

Fig. 1. Dependence of conductivity (**A**), activation energy (**B**) and thermoelectric e.m.f. (**C**) on irradiation dose and temperature of thermal treatment.

I— $7.2 \cdot 10^{22}$; *II*— $4.3 \cdot 10^{23}$; *III*— $1.5 \cdot 10^{24}$ eV/g

to $\sigma \sim 10^{-1} \Omega^{-1} \cdot \text{cm}^{-1}$ at t. t. o. 800° , with some slowing in the region 500 — 600° at 10^{-9} — $10^{-8} \Omega^{-1} \cdot \text{cm}^{-1}$. It is also evident that an increase in the dose of preliminary irradiation, i.e., an increase in the degree of radiation structuring, facilitates the subsequent pyrolytic transformations leading to changes in the electrophysical characteristics.

Fig. 2. Effect of oxygen on conductivity in a constant field (**A**) and on the thermoelectric e.m.f. (**B**) as a function of temperature. Dose $7.2 \cdot 10^{22}$ eV/g, t. t. o. 720° .

1, 3—in the presence of oxygen; 2, 4, 5—in vacuum

The temperature dependence of σ , studied in the range from -25° to $+150^\circ$, follows the relation $\sigma = \sigma_0 e^{-\Delta E/2KT}$ with a constant value of ΔE for each specimen. The curves in Fig. 1 represent the dependence of E on t. t. o. The change in ΔE is antipathetic to the change in σ with treatment temperature. In the same figure (**C**) the thermoelectric e.m.f. is presented for materials with t. t. o. from 620 to 930° . In this region the thermoelectric e.m.f. passes through values from 250 to $4 \mu\text{V}/\text{grad}$; in all cases the sign of the thermoelectric e.m.f. corresponds to *p*-type conductivity. The thermoelectric e.m.f. measured in

vacuum does not depend on the average temperature of the specimen in the range from -50° to $+150^\circ$ at $\Delta T = 7 \div 10^\circ$.

Oxygen has a substantial influence on all the indices presented. In its presence σ increases, the thermoelectric e.m.f. increases, and ΔE decreases. As shown for the product I_{720} in Fig. 2, this influence is manifested only up to a certain temperature, above which the behavior of vacuum and oxygen specimens becomes identical. This temperature is closely related

is associated with the depth of thermal modification of the material and decreases from 230° for a thermal-treatment temperature of 420° to 25° for a thermal-treatment temperature of 825° . All the indicated oxygen effects are strictly reversible.

Some information about the structural changes in the material responsible for the 15-order increase in σ_{dc} can be obtained by studying the conductivity in an alternating field.

Table 1 presents the resistivity of three samples as a function of frequency. As can be seen, the resistance decreases with increasing frequency, and at high frequencies in the range 5-12 MHz has the same value, $\sim 10^2 \Omega \cdot \text{cm}$, for all three samples.

Table 1

Sample No.	0	0.05	5.0	8.0	12.0	16.0
I_{420}	$\sim 2 \cdot 10^{11}$	$4.4 \cdot 10^5$	$2.5 \cdot 10^3$	$2.5 \cdot 10^2$	$1.5 \cdot 10^2$	$1.2 \cdot 10^2$
II_{520}	$\sim 1 \cdot 10^9$	—	$4 \cdot 10^2$	$2.5 \cdot 10^2$	$1.5 \cdot 10^2$	—
I_{805}	$\sim 1 \cdot 10^3$	—	$2.5 \cdot 10^2$	$1.5 \cdot 10^2$	$1.5 \cdot 10^2$	$1.2 \cdot 10^2$

This shows that the material is inhomogeneous and contains regions with high conductivity, $\sigma \sim 10^2 \Omega^{-1} \cdot \text{cm}^{-1}$, apparently characterized by polyconjugated structures and already appearing at low thermal-treatment temperatures. As the thermal-treatment temperature is increased, these domains grow at the expense of the surrounding interlayers with a less regular structure, which determine the conductivity in a constant field. Further development of ideas about the character of the gradual change in the structure of the polymer under radiation-thermal modification leads to the study of EPR spectra. Beginning with irradiated but not pyrolyzed polyethylene and up to the product with a thermal-treatment temperature of 920° , the spectrum consists of a single line, whose intensity, width, and shape differ in different cases. The concentration of paramagnetic centers and the line width do not depend on the measurement temperature.

Fig. 3. Dependence of the concentration of paramagnetic centers on the thermal-treatment temperature.

1— $4.3 \cdot 10^{23}$; 2— $1.5 \cdot 10^{24}$; *a*—air; *b*—vacuum.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 4. Dependence of the EPR line width on the thermal-treatment temperature. *a–b*, in the presence of oxygen in air; *b*—vacuum, $2 \cdot 10^{-3}$ mm Hg, 2 h; *v*— $5 \cdot 10^{-5}$ mm, 2 h; *g*— $5 \cdot 10^{-6}$ mm, 24 h.

In Fig. 3 the concentration of paramagnetic centers is presented as a function of the thermal-treatment temperature. In products with a thermal-treatment temperature $< 600^\circ$, the concentration of paramagnetic centers (p.m.c.) is the same in the presence and in the absence of O_2 ; like the conductivity, at a given thermal-treatment temperature it increases with an increase in the dose of preliminary irradiation. In products with a thermal-treatment temperature $> 600^\circ$, the concentration of p.m.c. drops sharply in the presence of O_2 —by 90% for a thermal-treatment temperature of 720° and to zero for products having a thermal-treatment temperature of 820° ; however, this effect is strictly reversible. Such a course of the curve is analogous to that described by a number of authors for various natural coals^(5, 6) and pyrolyzed organic compounds^(7, 8).

In Fig. 4, as a function of the heat-treatment temperature, the values of the line width are presented that correspond to various conditions of oxygen removal. The values ΔH obtained after pumping for 2 h at 10^{-3} mm Hg (standard pumping) lie on a curve with a sharp minimum at a heat-treatment temperature of $\sim 700^\circ$, analogous to the curves given for coals and pyrolysis products^(6–8). In the case of the polyethylene-transformation products investigated by us, this dependence appears to be seeming. With very thorough pumping (up to 24 h continuously at 10^{-5} – 10^{-6} mm Hg), in all samples, beginning with irradiated but nonpyrolyzed polyethylene, a line width $\Delta H = 0.5$ oersted is established. The broadening of the line to 7.5 oersted is therefore determined by the interaction of the unpaired electrons of the material with O_2 molecules, and not with the protons present in it.

Analysis of the signal shape by the method of linear anamorphoses⁽⁹⁾ shows that the line gradually changes from Lorentzian in the middle and Gaussian on the wings for nonpyrolyzed irradiated polyethylene and low heat-treatment temperatures to purely Lorentzian for high heat-treatment temperatures. This is interpreted as the presence, already before the start of thermal treatment, of isolated regions of predominantly exchange interaction, which, as the heat-treatment temperature is raised, increase in size at the expense of intermediate, less regular regions. When the delocalization regions are insufficiently developed, analysis of the line shape makes it possible to detect a dependence of the exchange frequency on temperature: at $+42^\circ$, the signals of samples III₇₂₀,

III₆₂₀, and III₅₅₀ have a Lorentzian shape, samples III₀ a mixed one, while at -196° the signals III₇₂₀ and III₆₂₀ retain a Lorentzian shape, whereas the signal III₅₅₀ changes to mixed, and III₀ to purely Gaussian.

In addition to temperature, oxygen affects the shape of the signals of samples with a low heat-treatment temperature. Sample III₂₇₀ changes at $+42^{\circ}$ from a mixed shape after 2 h pumping at 10^{-3} to a completely Lorentzian one after 24 h at 10^{-5} – 10^{-6} mm Hg. From this it may be concluded that the oxygen remaining in the first case affects the g -factors of individual regions, causing their probabilistic distribution. On the other hand, adsorbed oxygen facilitates exchange: indeed, in the case of sample III₀, the mixed shape at 42° is closer to Lorentzian in the presence of air than after standard pumping.

From the data presented it is evident that the influence of molecular oxygen on the e.p.r. spectra is manifold: 1) line broadening without a change in the number of paramagnetic centers, 2) influence on the g -factor, 3) facilitation of exchange, 4) blocking of paramagnetic centers in the case of heat-treatment temperatures $> 600^{\circ}$. To compare these effects with the influence of oxygen on conductivity and thermo-e.m.f. given above, further refinement of the data is necessary.

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CITED LITERATURE

1. M. Dole, D. C. Milner, F. F. Williams, *J. Am. Chem. Soc.*, **79**, 4809 (1957).
2. E. J. Lawton, J. S. Balwit, R. S. Powell, *J. Chem. Phys.*, **33**, 405 (1960).
3. F. H. Winslow, W. O. Baker, W. A. Yager, *J. Am. Chem. Soc.*, **77**, 4751 (1954).
4. V. G. Sidyak, E. T. Skoryk, *Pribory i tekhn. eksper.*, No. 2, 141 (1960).
5. D. E. G. Austen, D. I. E. Ingram, G. M. Tapley, *Trans. Faraday Soc.*, **54**, 400 (1958).
6. D. E. G. Austen, *Nature*, **174**, 797 (1954).
7. N. N. Tikhomirova, B. V. Lukin, L. L. Razumova, V. V. Voevodskii, *DAN*, **122**, 262 (1958).

8. S. Mrozowski, D. Wobshall, *J. Chim. Phys.*, **57**, 915 (1960).
9. N. N. Tikhomirova, V. V. Voevodskii, *Optika i spektroskopiya*, **7**, 829 (1959).

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