Reports of the Academy of Sciences of the USSR

A. V. VANNIKOV, G. N. DEMIDOVA, L. D. ROZENSHTEIN, N. A. BAKH

1965

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1965. Vol. 160, No. 3

PHYSICAL CHEMISTRY

A. V. VANNIKOV, G. N. DEMIDOVA, L. D. ROZENSHTEIN, N. A. BAKH

PHOTOCONDUCTIVITY OF ORGANIC SEMICONDUCTORS BASED ON POLYETHYLENE

(Presented by Academician A. N. Frumkin on 18 VII 1964)

As was shown earlier, the products of radiation-thermal treatment of polyethylene possess semiconducting properties ($^{1-3}$), which is associated with the appearance and growth of regions of polyconjugation in the polymer during its treatment. We set ourselves the task of detecting photoconductivity in these substances. The present work is devoted to the results of this study.

The method of preparing the samples is described in (^{1}). We investigated three samples, the first of which was not subjected to additional thermal treatment after preoxidation (sample 1), while the second (2) and third (3) were heated at 360 and 430° respectively. The samples were studied in a surface cell on quartz plates with gaps between platinum electrodes of 0.06–0.12 cm. For measurements of the electrical characteristics, the samples on the plates were placed in a quartz vessel evacuated to $\sim 10^{-5}$ mm Hg, in which the temperature of the sample could be varied over a wide range. Illumination was carried out through a window in the vessel made of optical fused quartz. The samples were illuminated with focused monochromatic light (quartz monochromator ZMR-3) from a xenon lamp DKSh-250. Like most photoelectrically sensitive organic semiconductors (dyes, polymers, polycyclic aromatic hydrocarbons), these objects are very high-resistance semiconductors. Therefore, for measurements of the dark current and photocurrent in them we used an EMU-3 electrometric amplifier with a current sensitivity of $1.5 \cdot 10^{-14}$ A/div. A voltage of 400 V was applied to the samples. Under these conditions we succeeded in observing photoconductivity in all three samples. The magnitude of the observed photocurrent was determined by the wavelength of the incident light and, for example, for $\lambda = 600$ mμ at room temperature lay for these samples within the range $2.2 \div 90 \cdot 10^{-14}$, and at an incident energy of ~ 6 mW/cm^2. In this case, for samples II and III the conductivity under illumination increased by approximately an order of

Fig. 1. Absorption spectra of treated polyethylene for samples 1, 2, 3. Fig. 2. Spectral curves of photoelectric sensitivity for the same samples.

Figure 1: Fig. 1. Absorption spectra of treated polyethylene for samples 1, 2, 3. Fig. 2. Spectral curves of photoelectric sensitivity for the same samples.

magnitude. Sample I was more highly resistive, and with the given electrode geometry we were unable to measure its dark conductivity reliably. However, it can be estimated that in this case also the factor by which the conductivity increased was not less than 10.

A general trend with increasing depth of thermal treatment of the samples is an increase in their dark and photoconductivity. At the same time, both of them (for 2 and 3) increase to approximately the same extent, so that the factor of change in conductivity upon illumination remains approximately constant. The measurements showed that up to the maximum applied voltage (400 V), Ohm' s law is obeyed for both the dark currents and the photocurrents. Over a wide range of illuminations the photocurrent depends linearly on the intensity of the incident light.

Figures 1 and 2 show the spectral curves of optical absorption and photoelectric sensitivity of the samples. As for a number of other

of such polymers, which contain systems of conjugated bonds (4), the absorption spectra of treated polyethylene are curves that decrease monotonically toward longer wavelengths over a broad spectral interval. This can be associated with the presence in the polymer of a set of conjugated regions of different sizes. As the heat treatment is intensified, the spectra shift toward longer wavelengths (Fig. 1). A similar shift was observed for films of the polymer tetra-cyanoethylene and is associated with an increase, during heat treatment of the polymer, in the relative content of more extended conjugated regions in it. Apparently, this is also true for treated polyethylene.

Fig. 1. Absorption spectra of treated polyethylene for samples 1, 2, 3
Fig. 2. Spectral curves of photoelectric sensitivity for the same samples

A long-wavelength shift is also observed for the spectra of photoelectric sensitivity of samples 1-3 (Fig. 2). Spectra 2 and 3 were measured at room temperature. For 1, because of its lower photoconductivity, the measurements were carried out at 140°. Curve 1 for this sample was obtained by extrapolating the measured spectrum to room temperature, taking into account the dependence of the photocurrent on temperature.

Fig. 3. Temperature dependences of dark and photoconductivity for samples 1-3: **a** –dark conductivity, **b** –photoconductivity at $\lambda = 800$ mμ, **c** –the same at $\lambda = 600$, **d** –546, **e** –500, **f** –400 mμ

The temperature dependences of dark and photoconductivity are presented in Fig. 3. As was established earlier (2), the dark conductivity of radiation-

Fig. 3. Temperature dependences of dark and photoconductivity for samples 1-3: a –dark conductivity, b –photoconductivity at $\lambda = 800$ mμ, c –the same at $\lambda = 600$, d –546, e –500, f –400 mμ.

Figure 2: Fig. 3. Temperature dependences of dark and photoconductivity for samples 1-3: a –dark conductivity, b –photoconductivity at $\lambda = 800$ mμ, c –the same at $\lambda = 600$, d –546, e –500, f –400 mμ.

thermally treated polyethylene changes with temperature according to an exponential law. The activation energies of the electrical conductivity of 2 and 3 are equal to 1.27 and 1.23 eV (calculated per $2kT$). As can be seen from Fig. 3, the same character of the temperature dependence also holds for photoconductivity. However, its activation energies (ε_ϕ) are significantly smaller. Thus, for sample 1, ε_ϕ (per kT) = 0.19 ($\lambda = 600$ mμ); 0.175 (546 mμ), 0.158 (500 mμ) and 0.150 eV (400 mμ). These data show that, as the wavelength of the incident light decreases, ε_ϕ decreases. In addition, for each wavelength ε_ϕ decreases on going to more highly treated samples. For example, for 546 mμ, $\varepsilon_\phi = 0.175$ (1), 0.095 (2), and 0.071 eV (3).

Proceeding from these regularities, one can apparently form the following picture of the process. During the decay of an exciton produced under the action of an absorbed light quantum, the carriers become trapped. To transfer them to the conduction level, additional thermal activation is required, which is manifested in the character of the temperature increase of the photocurrent (5). From this point of view it must be assumed that in the polymer there exists a distribution of traps by energy, and the larger the quantum, the more preferentially the current carriers are trapped in more highly situated traps. Then the necessary additional thermal energy (ε_ϕ) will decrease as the quantum energy increases. A decrease of the energy ε_ϕ on passing to more highly heat-treated samples should, in this case, indicate that with deeper heat treatment of the polymer the density of traps in it increases, in particular of those located close to the conduction level.

Institute of Electrochemistry
Academy of Sciences of the USSR

Institute of Semiconductors
Academy of Sciences of the USSR

Received
7 VII 1964

REFERENCES

[1] N. A. Bakh, V. D. Bityukov, A. V. Vannikov, A. D. Grishina, DAN, 144, 135 (1962). [2] A. V. Vannikov, N. A. Bakh, DAN, 149, 357 (1963). [3] A. V. Vannikov, DAN, 152, 905 (1963). [4] B. E. Davydov, I. A. Drabkina, Yu. V. Korshak, L. D.

Rozenshtein, Izv. AN SSSR, ser. khim., 1963, No. 9, 1664. [5] A. T. Vartanyan, ZhFKh, 20, 1065 (1946); 24, 1361 (1950).

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