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Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

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PHOTOCONDUCTOR PROPERTIES OF ACETYLENIC POLYMERS

In papers ([1,2]), the synthesis was described and some semiconductor properties of an entire class of poly-bis-acetylenes were investigated. The aim of the present work was to determine the presence of an internal photoeffect in polymers of this type. It should be noted that for a long time, in the laboratory of A. N. Terenin, searches were carried out for photoelectrically sensitive polymers. Polymers synthesized by various national schools ([3–5]) were studied. Measurements were performed by the usual method of photoconductivity under direct current and by the capacitor method under modulated illumination ([6]). Individual objects, in measurements of photoconductivity under direct current, showed an insignificant increase in conductivity under illumination. However, all the polymers tested did not show the presence of an alternating photo-e.m.f. detectable by the capacitor method. This indicates that the concentration of photocurrent carriers formed under illumination is small, and their mean free path is short. More than 100 different polymers were tested, with an invariably negative result.

Fig. 1. Spectral distribution of the photo-e.m.f. (in arbitrary units), referred to equal incident energy:
1 –polymer I, **2** –polymer II

In further development of these searches, polyacetylenes (I–VIII), synthesized in the laboratory of V. V. Korshak, were subjected to investigation; some of them (I–III) exhibited high photoelectric sensitivity in modulated light (300 cps). At energies of 10^{-4}–10^{-6} W/cm^2 beyond the exit slit of the monochromator, the value of the photo-e.m.f. at the maximum was 10 mV/mW. Polymers IV–VI possessed lower photosensitivity. In polymers VII–VIII no photo-e.m.f. was detected.

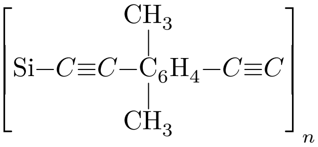
The sign of the photocurrent carriers, determined by the capacitor method in combination with a synchronous detector (⁷), indicated the hole character of the photocurrent for samples I—IV. Samples of polymers V—VI gave a negative sign of the photocarriers. All the polymers investigated were powders. With the aid of a monochromator with a diffraction grating (aperture ratio 1:4) and a xenon lamp as the source, spectral curves of the photoelectric sensitivity of polymers I, II were recorded; these are shown in Fig. 1.

On the photo-e.m.f. curve of polymer I (Fig. 1, 1), on the decline there is a selective maximum at $\lambda = 480$ mμ of exciton type. Polymer II gives, in the same region, a broader selective maximum (Fig. 1, 2). The measurements described above were carried out in air. Measurements in vacuum (10^{-4} mm Hg) showed that the spectral curve does not undergo any substantial change in its form.

$$\mathrm{C_6H_5{-}C{\equiv}C{-}}\left[-\mathrm{C{\equiv}C{-}}\substack{\text{anthracene nucleus}\\ \text{with HO and OH}}-\mathrm{C{\equiv}C{-}}\right]_{\mathrm{n}}\mathrm{C{\equiv}C{-}C_6H_5} \qquad \text{(I)}$$

$$[-C{\equiv}C{-}\mathrm{C_6H_4}{-}N{=}N{-}\mathrm{C_6H_4}{-}C{\equiv}C{-}]_n \qquad \text{(II)}$$

$$\mathrm{C_6H_5{-}C{\equiv}C{-}\,[C{\equiv}C{-}C_6H_4{-}C{\equiv}C]_n\,C{\equiv}C{-}C_6H_5} \qquad \text{(III)}$$



$$\left[\mathrm{Si}{-}C{\equiv}C{-}\underset{\mathrm{CH_3}}{\overset{\mathrm{CH_3}}{\mathrm{C_6H_4}}}{-}C{\equiv}C\right]_n \qquad \text{(IV)}$$

$$[C{\equiv}C]_n \qquad \text{(V)}$$

$$\left[-C{\equiv}C{-}\substack{\text{anthracene nucleus}\\ \text{with HO and OH}}-C{\equiv}C{-}\right]_n [C{\equiv}C]_m \qquad \text{(VI)}$$

methyl-substituted pyridine ring$\mathrm{{-}C{\equiv}C{-}}$ $\mathrm{[C{\equiv}C{-}}$dimethyl-substituted pyridine ring$\mathrm{{-}C{\equiv}C]_n}$ $\mathrm{C{\equiv}C{-}}$methyl-sub
(VII)

$\mathrm{CH_2OH{-}C{\equiv}C{-}}$ $\mathrm{[C{\equiv}C{-}}$dimethyl-substituted pyridine ring$\mathrm{{-}C{\equiv}C]_n}$ $\mathrm{C{\equiv}C{-}CH_2OH}$
(VIII)

In the course of the work, attention was drawn to the fact that preliminary irradiation of the samples with the full UV light of an SVD-120 mercury lamp considerably increases the photo-emf signal. Thus, for example, irradiation of polymer II for 2 h made it possible to increase its photosensitivity by an order of

Fig. 2

Figure 2: Fig. 2

magnitude. Isolation, by means of light filters, of definite regions of the mercury-lamp spectrum showed that the long-wavelength threshold for activation of the photo-emf lies at 366 mμ; the 405 mμ line is inactive. In compensating for the different intensities of the mercury lines and the transmission coefficients of the light filters, different exposures were used (from 1 to 30 min). It was established that, depending on the irradiation time, the behavior of the activated photo-emf in different polymers is not the same.

Figure 2 shows the kinetics of the change in the photo-emf as a function of the time of irradiation by the full light of the SVD-120 mercury lamp for polymer I. Irradiation was carried out in vacuum (Fig. 2, 1) and in air (Fig. 2, 2). When the sample was irradiated in vacuum, activation of the photo-emf proved more effective than when irradiation was carried out in air. It is interesting that, upon illumination of polymer I, the photo-emf increases for 3–5 min and then begins to decrease and, after approximately one hour of exposure, reaches its initial value. After the polymer has remained in air in the dark for 1-2 h, the entire process can be repeated again, i.e., the phenomenon is completely reversible.

The character of the change in the photo-emf under the action of UV light for polymer II is shown in Fig. 3. In the course of working with polymer II it was established,

that admitting air to a sample activated in vacuum instantly lowers the photo-emf by a factor of 2-3. The fact that the internal photoeffect in a hole-type semiconducting polymer is quenched by air (oxygen) proved unexpected. The process of activation by ultraviolet light and quenching of the photo-emf by air in polymer II can be reproduced repeatedly. Electron semiconducting polymers (V, VI), owing to their low photosensitivity, could not be subjected to as detailed an analysis as I and II.

Fig. 2. Change in photo-emf (in arbitrary units) as a function of the time of illumination with ultraviolet light from an SVD-120 lamp for polymer I: **1**—in air; **2**—in a vacuum of 10^{-4} mm Hg.

At this stage of the investigation, the following preliminary interpretation of the results may be proposed. The polymers studied, like most organic semiconductors (^{8}), have a hole type of photoconductivity.

Photoactivation of the polymer by ultraviolet irradiation with $\lambda = 366$ m , which, upon subsequent illumination with long-wavelength light (threshold $\lambda = 600$ m), leads to the appearance of hole carriers of photocurrent, may have the following explanation. Ultraviolet light ionizes the conjugated molecules making up the polymer, creating positively charged local centers that can serve as traps for electrons; the liberated photoelectron is retained in the polymer structure.

Fig. 3

Figure 3: Fig. 3

Such a prolonged trapping of electrons during photoionization in organic media at low temperature, leading to a quadratic law of phosphorescence decay, is known ([9]). The mechanism of hole photoconductivity in polymers under the action of long-wavelength light is evidently the same as in numerous organic semiconducting dyes ([8,10]). Absorption of light by the ordered molecular system causes the appearance of an exciton migrating between molecules. On reaching defects, whose formation is also favored by ultraviolet illumination, the exciton is destroyed with formation of an electron captured by the defect and a mobile hole. The rigidity and extension

Fig. 3. Change in photo-emf (in arbitrary units) as a function of the time of illumination with ultraviolet light from an SVD-120 lamp for polymer II.

the conjugated bond in the polymer units favors the free path of the photocurrent charge carrier.

The significant photosemiconductor sensitivity found for these polymers, in our opinion, points to ways of approaching the problem of synthesizing photosensitive polymers.

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