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Abstract

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PHOTOCONDUCTIVITY OF ACETYLENE POLYMERS

Recently, in the laboratory of V. V. Korshak, a number of polymers containing an acetylene bond in the macromolecule have been synthesized ([1],[2]), and their dark semiconductor properties have been studied ([3]). In an earlier paper ([4]) in our laboratory, an internal photoeffect was discovered in some polymers of this type. The investigations were carried out by the capacitor method ([5]-[8]), with a light-flux modulation frequency of 300 cps. In a subsequent paper ([9]) the presence of photoconductivity in polymers of the same type was established, and the relaxation of photoconductivity was studied by the "tau-meter" method in the time interval from $1 \cdot 10^{-5}$ to $1 \cdot 10^{-2}$ sec. The presence of a short-time component of the photocurrent (10^{-5} sec) indicates the electronic nature of the processes, while the established hyperbolic law of decay of the photocurrent points to the bimolecular character of photoconductivity relaxation.

The present work is a continuation of the investigation of the basic regularities of the photoconductivity of acetylene polymers, using as an example poly-*n*—*n*-diethynylazobenzene

$$(-\mathrm{C} \equiv \mathrm{C} - \mathrm{C_6H_4} - \mathrm{N} = \mathrm{N} - \mathrm{C_6H_4} - \mathrm{C} \equiv \mathrm{C}-)_n \, .$$

The polymer was synthesized at the Institute of Organoelement Compounds of the Academy of Sciences of the USSR and was kindly provided to us by V. V. Korshak and A. M. Sladkov.

Transverse photoconductivity was measured at constant voltage and constant illumination with an EMU-3 amplifier equipped with a set of input resistances. A suspension of the polymer in dimethylformamide was applied to a quartz plate with a cathode deposit sprayed on it, and then platinum electrodes were fused into it. The latter had the form of two "combs," each with 10 teeth, with a distance between neighboring teeth of 0.1 mm. The dimethylformamide was then evaporated. The thickness of the layers was 1-5 μ. It should be noted that measurement of photoconductivity encountered certain difficulties owing to the large temperature coefficient of the polymer resistance. Therefore, for thermostating, the quartz plate, 1 mm thick, bearing the electrodes was pressed against the flat polished face of a glass finger, which was filled with water at 17° and was located inside a glass vessel with a quartz window for illuminating the polymer layer. A voltage of 100–200 V was applied to the photoresistance electrodes. For undecomposed condensed illumination, an SVD-110 mercury lamp and a 70 W incandescent lamp were used. A heat filter, consisting of a quartz cuvette with water 5 cm thick, was placed in front of the sample. The spectral distribution of photoconductivity in the region 300–1000 mμ was measured with a high-aperture (1:5) monochromator with a diffraction grating. The spectra were reduced to an equal-energy value. The spectral distribution of the radiation of a GSV D-120 xenon lamp beyond the exit slit of the monochromator was measured with a calibrated thermoelement and varied over the spectrum from 10^{12} to 10^{15} quanta/sec. The duration of exposure of the polymer sample at each photocurrent reading was 1.5 min. Dark

the pause between illuminations was 3–4 min. The input resistance of the amplifier was chosen to be 2 orders of magnitude smaller than the resistance of the polymer layer under illumination. The dependence of the photocurrent on illumination was checked using a set of neutral light filters. The reflection spectra of the polymer were measured on an SF-4 spectrophotometer.* The dark resistance of the layers was 10^{12} Ω and higher. For stable photocurrent readings, all measurements were carried out on samples formed by current at a voltage of 100–200 V for 10–15 h, after which the resistance of the polymer decreased by a factor of 5–8.

When a freshly prepared polymer layer was illuminated with the integral light of an incandescent lamp, the photoconductivity was insignificant. The dark resistance exceeded the light resistance by a factor of 3–5. If the sample was illuminated with the full light of an SVD-110 mercury lamp, the photoconductivity increased, and the change in resistance amounted to 2–3 orders of magnitude. A polymer preliminarily irradiated with the full light of an SVD-100 mercury lamp exhibited considerable photoconductivity also under irradiation by an incandescent lamp. In order to clarify the nature of the phenomenon, measurements were made of the spectral distribution of photoconductivity. The spectra were recorded in the region of linear dependence on illumination.

In Fig. 1,1 (1) a typical curve is given for the spectral distribution of the photoconductivity of a polymer layer not subjected to preliminary exposure to ultraviolet light. Two selective maxima are observed on the curve, at 330 and 610 mµ. The spectrum in this case was measured starting from long wavelengths. We note that as the spectrum was recorded, the sample became more photosensitive. If, after measuring the spectrum beginning with long wavelengths, the spectrum is measured a second time beginning with short wavelengths (300 mµ), then the intensity of the maximum in the region of 610 mµ increases.

To reveal more clearly the influence of ultraviolet exposure, the polymer layer was exposed for several minutes to the full light of a mercury lamp, and then the spectrum was measured beginning with long wavelengths. In Fig. 1,2 the photoconductivity spectrum of the polymer immediately after irradiation with the light of a mercury lamp is shown. The curve clearly shows a redistribution of intensities between the short-wavelength and long-wavelength maxima. In this case the long-wavelength maximum retains its position at 610 mμ, while the maximum at 330 mμ shifts into the long-wavelength region. This shift depends on the total energy of the incident light and on the exposure time. It was possible to obtain samples in which the short-wavelength maximum shifted to 400 mμ. The effect of redistribution of the heights of the photoconductivity maxima is partially reversible.

It follows from Fig. 1,2 that, during prolonged measurement of the spectrum (2 h), the ratio of the long-wavelength maximum to the short-wavelength maximum is $3:2$. If, however, the photocurrent readings at two wavelengths (610 and 360 mμ) are compared immediately after illumination with ultraviolet light, then the long-wavelength maximum exceeds the short-wavelength one by a factor of 3–4. However, even after prolonged storage in the dark, complete return to the photoconductivity spectrum of the unexposed polymer is not observed. Upon irradiation, the color of the polymer changes from red-orange to brown-red. If, according to Moss (^{8}), the optical activation energy of conduction (E) is determined from the value of $\frac{1}{2}\lambda_{\text{max}}$, then for the polymer studied one obtains $E = 1.82 \pm 0.02$ eV.

Activation of the photoeffect (photo-e.m.f.) by ultraviolet light was noted by us in work (^{4}), where it was indicated that the activation is completely reversible in character. Additional experiments carried out by the capacitor method showed that the reversibility of the photo-e.m.f. is only partial, which agrees with the results on photoconductivity. In the same work (^{4}) it is reported

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* The authors express their gratitude to A. S. Topor for measuring the reflection spectra.

spectral distribution of the diffusion photo-e.m.f. for the same polymer.

Figure 1, 3 gives the spectral curve of the diffusion photo-e.m.f. for a polymer layer after preliminary 10-minute exposure to the integral light of a mercury lamp. Before the measurement of the capacitor photo-e.m.f., the polymer powder was kept for several hours in dimethylformamide in order to make the conditions identical to those for measuring photoconductivity. The experiments showed that this factor has no substantial significance. From the curves (Fig. 1) it follows that the photoconductivity spectrum is shifted into the long-wavelength region relative to the photo-e.m.f. spectrum. Such a shift has repeatedly been observed for inorganic and organic semiconductors $^{(11-13)}$. A sharp difference in the spectral distribution of the photo-e.m.f. and photoconductivity is observed in the long-wavelength part of the spectrum. Whereas in the photo-e.m.f. spectrum only a maximum in the region of 500 mμ is barely indicated, in the photoconductivity spectrum it is sharply expressed (610 mμ). The presence of a maximum at 610 mμ can readily be explained if one takes into account the course of the absorption spectrum of this polymer. In Fig. 1, 4 the course of the polymer absorption spectrum is given, estimated from the spectral distribution of reflection $(1 - R_\lambda)$. It is seen from the curve that the photoconductivity

Fig. 1. Spectral distribution: 1 –photoconductivity for a polymer layer; 2 –the same after preliminary exposure of the layer to ultraviolet light (10 min.); 3 –photo-e.m.f. of the polymer after preliminary exposure to ultraviolet light (10 min.); 4 –reflection spectrum of the unexposed polymer.

Figure 1: Fig. 1. Spectral distribution: 1 –photoconductivity for a polymer layer; 2 –the same after preliminary exposure of the layer to ultraviolet light (10 min.); 3 –photo-e.m.f. of the polymer after preliminary exposure to ultraviolet light (10 min.); 4 –reflection spectrum of the unexposed polymer.

maximum at 610 mμ is observed on the decline of the absorption curve.

Fig. 1. Spectral distribution: **1** –photoconductivity for a polymer layer; **2** –the same after preliminary exposure of the layer to ultraviolet light (10 min.); **3** –photo-e.m.f. of the polymer after preliminary exposure to ultraviolet light (10 min.); **4** –reflection spectrum of the unexposed polymer.

The presence of a photoconductivity maximum on the decline of absorption is typical of photoelectrically sensitive semiconductors and is determined by the character of surface and bulk recombination of photocarriers.

In work (4) it was shown that holes serve as the carriers of photocurrent in this polymer. Obviously, under the action of ultraviolet light, centers capable of trapping electrons* are created in the polymer. It is precisely these centers that are responsible for the increase in photoconductivity in the red part of the spectrum under the action of ultraviolet radiation. The increase in the photoconductivity of polymers under ultraviolet illumination may also be promoted by the occurrence of further photopolymerization. It is possible that precisely this process causes the shift of the short-wavelength photoconductivity maximum into the long-wavelength region of the spectrum and the deepening of the color of the polymer. We note that Reed and Wesselsberg observed the formation of unstable high-molecular compounds from aromatic monomers with an acetylene bond upon irradiation with a mercury lamp and even proposed using the effect of a change in the color of substances under irradiation in offset printing** (12). It may be assumed that the mechanism of photoconductivity in polymers is the same as in photoconducting organic dyes (15,16). The primary act is the excitation of a polymer macromolecule by an absorbed photon. The excited state (exciton) migrates along an ordered series of molecules until it encounters some defect or center, at which the formation of a free photocurrent carrier occurs; this carrier migrates along the chain of polymer macromolecules.

Received

* The presence of such centers is confirmed by the electron-paramagnetic-resonance signal in this polymer detected in our laboratory by E. V. Baranov.

** A. M. Sladkov kindly drew our attention to this work.

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