# THE INTERNAL PHOTOEFFECT IN ACETYLENE POLYMERS

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## Abstract

## Full Text

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# THE INTERNAL PHOTOEFFECT IN ACETYLENE POLYMERS

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Recently a number of works have appeared devoted to the study of the photoelectric properties of polymers with conjugated bonds and heteroatoms in the conjugation chain ($^{1-5}$). The internal photoeffect in polyacetylene compounds has been discovered and is being investigated in our laboratory ($^{6-10}$). As a continuation of these investigations, the present work reports on the photosemiconducting properties of a number of new acetylene polymers. The following compounds were studied: a copolymer of *p*-diethynylbenzene and *p*-nitrophenylacetylene (I); a compound obtained by reduction with zinc dust of copolymer I (II); the product of joint polycondensation of 9,10-diethynylanthracene with *p*-nitrophenylacetylene: soluble fraction (III), insoluble fraction (IV); the product of joint polycondensation of 9,10-diethynyl-9,10-dioxy-9,10-dihydroanthracene with *p*-nitrophenylacetylene: soluble fraction (V), insoluble fraction (VI); the product of joint polycondensation of 9,10-diethynyl-9,10-dioxy-9,10-dihydroanthracene with $\alpha$-naphthylacetylene (1 : 1): soluble fraction (VII), insoluble fraction (VIII); the product of joint oxidative condensation of *p*-diethynylbenzene and the dipropargyl ether of 4,4′-dioxydiphenyl (IX)*. The structure of the polymers is characterized by aggregation into bundles of parallel molecular chains with high azimuthal ordering, depending on the incorporation into the chain of orienting phenyl and anthracene groups ($^{12}$).

I $\mathrm{NO_2{-}C_6H_4{-}C{\equiv}C{-}\,[{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}]_n\,{-}C{\equiv}C{-}C_6H_4{-}NO_2}$

III-IV $\mathrm{NO_2{-}C_6H_4{-}C{\equiv}C{-}\,[{-}C{\equiv}C{-}anthracene{-}C{\equiv}C{-}]_n\,{-}C{\equiv}C{-}C_6H_4{-}NO_2}$

V-VI $\mathrm{NO_2{-}C_6H_4{-}C{\equiv}C{-}\,[{-}C{\equiv}C{-}9{,}10\text{-}dihydroxy\text{-}9{,}10\text{-}dihydroanthracene{-}C{\equiv}C{-}]_n\,{-}C{\equiv}C{-}C_6H_4{-}NO_2}$

VII-VIII $\mathrm{naphthyl{-}C{\equiv}C{-}\,[{-}C{\equiv}C{-}9{,}10\text{-}dihydroxy\text{-}9{,}10\text{-}dihydroanthracene{-}C{\equiv}C{-}]_n\,{-}C{\equiv}C{-}naphthyl}$

Fig. 1

Figure 1: Fig. 1

IX $[-C{\equiv}C-C_6H_4-C{\equiv}C-]_m[-C{\equiv}C-CH_2-O-C_6H_4-C_6H_4-O-CH_2-C{\equiv}C-]_n$

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* The listed polymers were synthesized at the Institute of Organoelement Compounds of the Academy of Sciences of the USSR, in the laboratory of V. V. Korshak, by A. M. Sladkov and co-workers (11).

The internal photoeffect was studied by the method of diffusion photo-emf and transverse photoconductivity in air and in vacuum ($10^{-4}$—$10^{-5}$ mm). The measurement technique is described in papers (7–9). The spectral curves of photoconductivity were reduced to an equal number of quanta. When integral light was used, a heat filter was placed in front of the sample. To eliminate a possible light-filter effect when recording photoconductivity spectra, illumination was carried out from the electrode side.

Photoconductivity spectra were recorded point by point, starting from long wavelengths. In doing so, after each point the time necessary for attainment of the stationary dark conductivity was allowed to elapse. For the polymers whose photoconductivity spectra are presented, the rise time of the photoconductivity to its stationary value was usually 10–60 sec, and the decay time 1–3 min. The absorption spectra of solutions and polymer films were recorded on a UNICAM SP-700 spectrophotometer.

**Fig. 1.** 1 –spectral distribution of the photoconductivity of the product of the joint oxidative condensation of *p*-diethynylbenzene and dipropargyl ether of 4,4′-dioxydiphenyl (polymer IX); 2 –the same after 5 min irradiation with the integral light of an SVD-120 mercury lamp ($\lambda > 300$ nm); 3 –the same after 1 h irradiation.

In all polymers (I–IX), upon illumination with integral light from an SVD-120 mercury lamp, a photo-emf was observed in the visible and UV regions of the spectrum. In this case the sign of the predominant photocarrier was positive for all the compounds studied. It should be noted that, with respect to the integral light of the SVD-120 lamp, the magnitude of the photo-emf in soluble polyacetylenes (III, V, VII) is smaller than in the corresponding insoluble ones (IV, VI, VIII), which is naturally explained by the less pronounced delocalization of electrons in the former case.

As for the polyacetylenes studied earlier (1), the magnitude of the photo-emf increases during irradiation of the samples with light. During exposure the photoconductivity also changes. As an illustration, Fig. 1 gives the spectral

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

photoconductivity curves of polymer IX. Curve 1 represents the photoconductivity spectrum of a layer recorded from the long-wavelength side. The time required to measure the spectrum was 1.5 h. A slight change in photosensitivity occurs in the course of the comparatively weak exposure by monochromatic light during recording of the spectrum. This effect is manifested more clearly if the sample is irradiated with the integral light of an SVD-120 mercury lamp. The photoconductivity spectrum for the same layer of polymer IX, but after 5 min irradiation with the full light of a mercury lamp, is shown by curve 2. On irradiation through a BS-4 filter, radiation shorter than 300 nm was cut off.

After 1 hour of irradiation under the same conditions, the photoconductivity spectrum is shown by curve 3. As is seen from the figure, exposure of the polymer at first leads to an increase in photoconductivity, and then to its decrease. At the same time, the form of the spectral distribution of photoconductivity changes. The change occurs mainly through a redistribution of the intensity ratio between the individual maxima, which indicates that no new products are formed in the course of exposure of polymer IX, but only a change in the quantitative ratio between them occurs. The optical activation energy of the photoconductivity of IX, determined by the Moss method (13) from the photoconductivity spectrum, is 2.30±0.05 eV. It should be noted that after irradiation of IX the character of the photocurrent relaxation curves changes. As a rule, after prolonged irradiation the photoresponse becomes more inertial.

**Fig. 2.** Spectral distribution of the photoconductivity of the copolymer of *p*-diethynylbenzene and *p*-nitrophenylacetylene

**Fig. 3.** Absorption spectrum of a solution of the copolymer of *p*-diethynylbenzene and *p*-nitrophenylacetylene in dimethylformamide (1) and of a solid film (2)

Figure 2 gives the photoconductivity spectrum of compound I. The photoconductivity decreases smoothly with increasing wavelength and has a maximum in the region of 480–500 nm. It should be noted that the intensity of this maximum varied from layer to layer. The question of its nature requires additional investigation. The optical activation energy of the photoconductivity of IX is $2.33 \pm 0.05$ eV.

Pumping the air out of the vessel led to a decrease in the dark conductivity and photoconductivity of polymer I, which, in the case of a hole semiconductor, which, as indicated above, I is, is naturally explained by the acceptor action of oxygen for the conduction electrons.

It is of interest to compare the spectral distribution of the photoconductivity of I with the absorption spectrum of a film and of a solution of polymer I. Figure 3 shows the absorption spectrum of a solution of I in dimethylformamide (1) and the absorption spectrum of a film prepared from a solution of I in dimethylformamide. From a comparison of the absorption spectra of I in different states it is seen that, on going to the film, the absorption bands of the individual molecules are strongly broadened. At the same time, the absorption in the short-wavelength region of the spectrum increases sharply, which suggests the presence of a delocalized system of electrons participating in the absorption.

The photoconductivity spectrum I (Fig. 2) essentially reproduces the absorption spectrum of the solid film of polymer I, with the exception of the maximum at 480–500 nm.

As is known, in low-molecular organic semiconductors, for example anthracene ([1]), tetraphenylporphine ([15]), and dyes ([16,17]), on passing from solutions to the solid phase, strong intermolecular interaction leads to a broadening of the electronic absorption bands characteristic of individual molecules in solution, but the similarity of the spectra of the condensed phase and of the solution is preserved; this confirms the presence of valence-saturated molecules or molecular ions in the aggregated state. The spectral distribution of photosensitivity in low-molecular organic semiconductors reproduces the absorption spectrum in the solid phase ([14–17]). Such a relationship between the spectra of solutions, the solid phase, and photosensitivity, as is known, is one of the reasons why the question of the possibility of applying the band model to low-molecular organic semiconductors is debatable. In any case, if there is partial collectivization of the electrons of individual molecules with the formation of common energy bands for the whole crystal as a whole, then such specific energy bands of levels have a small width and do not appear in the spectra of low-molecular organic semiconductors. Therefore, possible mechanisms of photoconductivity in low-molecular organic semiconductors may be a hopping process of charge-carrier transfer from one molecule to another ([16–17]) and an exciton mechanism ([14]).

The relationships we have obtained between the absorption spectrum of the solid phase and that of the polymer solution, as well as the fact that the course of the photoconductivity spectrum I basically coincides with the course of the absorption spectrum of the solid film, may apparently be regarded as one of the experimental facts supporting the assertion that in the solid polymer I there exist collectivized energy bands for electrons, encompassing all molecules, and, consequently, with certain limitations, one may speak of the applicability of the band scheme to polyacetylene I.

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