



---

Soviet-era science, translated into English

# PHYSICAL CHEMISTRY

V. S. MYL' NIKOV

1963

SovietRxiv

---

View the original and related papers at <https://sovietrxiv.org/items/ru-196301.04736>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

**Abstract**

**Full Text**

## PHYSICAL CHEMISTRY

V. S. MYL' NIKOV

### KINETICS OF THE PHOTOCONDUCTIVITY OF ACETYLENE POLYMERS

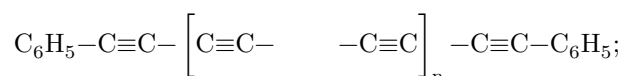
*(Presented by Academician A. N. Terenin, August 27, 1962)*

Recently, the study of the semiconducting properties of polymers with systems of conjugated bonds and heteroatoms in the conjugation chain has become widespread (<sup>1-4</sup>). The main attention has been devoted to the study of the electrical conductivity and electron paramagnetic-resonance signals of such polymers. There is practically no information in the literature on the photo-semiconducting properties of polymers.

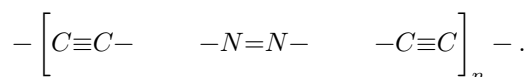
Searches for an internal photoeffect in polymers were carried out for a long time in the laboratory of A. N. Terenin. A large number of polymers of various classes were investigated, with an invariably negative result. The internal photoeffect was discovered by the capacitor method (<sup>5-7</sup>), under modulated illumination, in powders of a narrow class of acetylene polymers (<sup>8</sup>).

The aim of the present work was to detect photoconductivity in polyacetylenes and to study its relaxation. Two polymers synthesized in the laboratory of V. V. Korshak (<sup>9-11</sup>)\* were investigated, namely:

I



II



Polymer I is the product of the joint oxidative dehydropolycondensation of *p*-diethynylbenzene and phenylacetylene (1 : 1).

The polymers under investigation were deposited from a dimethylformamide solution onto quartz substrates, on the surfaces of which platinum electrodes had been evaporated in the form of two combs with gaps of 0.1 mm. The thickness of the layers was several microns. A constant voltage of 400 V was applied to the electrodes of such a photoresistor. Illumination was carried out

Figure 1

Figure 1: Figure 1

with the undecomposed light of a quartz mercury lamp DRSh-250 at a current of 3 A, with a modulation frequency of 100 Hz. The cutoff time, with a slit width of 2 mm, was  $4 \cdot 10^{-5}$  sec. A glass heat filter was placed in front of the sample; i.e., the effective wavelengths were limited to the region 350–600 m $\mu$ . Under these conditions, photoconductivity was observed in polymers I and II. The magnitude of the photocurrent was  $10^{-10}$ – $10^{-12}$  A.

In order to clarify the nature and mechanism of the phenomenon, the relaxation of photoconductivity was studied at the initial stages of the process. The investigation was carried out by the tautomer method<sup>(12)</sup> at constant voltage and modulated illumination. The instrument made it possible to observe the processes of rise and decay of the photocurrent in the time interval from  $1 \cdot 10^{-5}$  to  $1 \cdot 10^{-2}$  sec. The experiments were carried out in air and in vacuum ( $10^{-4}$ – $10^{-5}$  mm).

1. The study of the relaxation curves of photoconductivity in air at 20° for polymer I showed that, during an illumination time of the order of  $10^{-2}$  sec, the photocurrent does not have time to reach its stationary value. In Fig. 1A typical oscillograms of the change of photocurrent with time are shown for

---

\* The author expresses gratitude to V. V. Korshak and A. M. Sladkov for providing the polymer samples.

of polymer I in linear (a) and exponential (b, c) sweeps in air at 20°. Using an exponential sweep, on the initial portion of the rise and decay of the photocurrent one can distinguish an exponent (Fig. 1A, b) with a time constant of  $3 \pm 1 \cdot 10^{-5}$  sec. The half-life time of the process  $\tau_{ph}$  was

Fig. 1. Photoconductivity kinetics of polymer I. *A*—in air; *B*—in vacuum. *a*—linear sweep; *b, c*—exponential sweeps;  $\tau_{decay} = 3 \cdot 10^{-5}$  sec. (b);  $\tau_{ph} = 4 \cdot 10^{-3}$  sec. (c, in air);  $\tau_{ph} = 3 \cdot 10^{-3}$  sec. (c, in vacuum)

$4 \pm 1 \cdot 10^{-3}$  sec. (Fig. 1A, c). Using the method of “partial” relaxation times<sup>(13)</sup>, an analysis of the photocurrent-decay curves was carried out. It was established that the relaxation of photoconductivity is well described by a hyperbolic dependence

$$\Delta\sigma = \frac{\Delta\sigma_0}{(1 - at)^\alpha}. \quad (1)$$

In Fig. 2, 1 the decay of the photocurrent for polymer I in air is shown, measured on a tautomer by the method of “partial” times. In Fig. 2, 1' is shown the

Figure 2

Figure 2: Figure 2

Figure 3

Figure 3: Figure 3

dependence of the specific slowness of relaxation  $\theta^*$  on time. Analysis of the curves presented showed that the decay of the photocurrent in polymer I in air obeys the hyperbolic dependence (1) with constants  $\alpha = 0.435 \pm 0.007$  and  $a = 1.6 \pm 0.2 \cdot 10^{-3} \text{ sec}^{-1}$ . When polymer I is placed in vacuum, the photocurrent becomes less inertial (Fig. 1B, a). As in air, at the beginning of the rise and decay curve of the photocurrent one can distinguish an exponent with a time constant of  $3 \pm 1 \cdot 10^{-5} \text{ sec}$ . (Fig. 1B, b). The half-life time of the process in vacuum was  $3 \pm 1 \cdot 10^{-3} \text{ sec}$ . (Fig. 1B, c). Analysis of the photocurrent-decay curves showed that in vacuum the hyperbolic law (1) remains valid. In this case, at the very beginning of the photocurrent-decay process, up to times of  $3 \cdot 10^{-4} \text{ sec}$ ., the degree of the hyperbola decreases ( $\alpha = 0.15 \pm 0.06$ ) (Fig. 2, 2') in comparison with the value in air, which indicates a decrease in the inertia of the photocurrent in vacuum. At longer

Fig. 2. Decay of the photocurrent in polymer I in exponential sweep: 1—in air, 2—in vacuum. “Instantaneous” relaxation times in polymer I: 1'—in air, 2'—in vacuum

\* The quantity  $\theta$ , equal to the reciprocal logarithmic derivative of the photocurrent, taken with the opposite sign.

times ( $3 \cdot 10^{-4}$ — $20 \cdot 10^{-4} \text{ sec}$ .) the degree of the hyperbola changes only slightly ( $\alpha = 0.38 \pm 0.6$ ). The constant  $a$  for the first and second sections is, respectively:  $a_1 = 8.3 \pm 0.5 \cdot 10^{-3} \text{ sec}^{-1}$ ,  $a_2 = 1.4 \pm 0.3 \cdot 10^{-3} \text{ sec}^{-1}$ . In the preceding work<sup>(8)</sup> it was established that the carriers of the photocurrent in polymer I are holes. This is confirmed in the present case by the effect of air (oxygen) on the photoconductivity: admission of air into the vacuum vessel led to an increase in the photocurrent by several times.

**Fig. 3.** Kinetics of photoconductivity of polymer II. *A*—in air; *B*—in vacuum. *a*—linear sweep; *b, c*—exponential sweeps;  $\tau_{\text{decay}} = 1 \cdot 10^{-4} \text{ sec}$ . (*b*),  $\tau_{\text{pzh}} = 5 \cdot 10^{-3} \text{ sec}$ . (*c*, in air);  $\tau_{\text{pzh}} = 4 \cdot 10^{-3} \text{ sec}$ . (*c*, in vacuum)

2. Figure 3 shows the change of the photocurrent with time for polymer II in the linear (*a*) and exponential (*b, c*) sweeps in air (*A*) and in vacuum (*B*). The initial part of the photocurrent decay both in air and in vacuum is approximated by an exponential with time constant  $\tau = 2 \pm 1 \cdot 10^{-4} \text{ sec}$ . (Fig. 3b). The half-life of the process in air and in vacuum was, respectively,  $5 \pm 1 \cdot 10^{-3}$  and  $4 \pm 1 \cdot 10^{-3} \text{ sec}$ . (Fig. 3b). The decay of the photocurrent (Fig. 4) obeys the hyperbolic dependence (1). In air the law of photocur-

Figure 4

Figure 4: Figure 4

rent decay can be expressed as the sum of two hyperbolas (Fig. 4, 1') with constants:  $\alpha_1 = 0.094 \pm 0.011$ ,  $\alpha_2 = 0.42 \pm 0.07$ ,  $a_1 = 1.3 \pm 0.4 \cdot 10^{-4} \text{ sec}^{-1}$ ,  $a_2 = 1 \pm 0.3 \cdot 10^{-3} \text{ sec}^{-1}$ . In vacuum these two hyperbolas practically reduce to one (Fig. 4, 2') with constants  $a = 0.55 \pm 0.07$ ,  $a = 1.2 \pm 0.3 \cdot 10^{-3} \text{ sec}$ . The presence in air, for polymer II, of a hyperbola with a smaller degree than in vacuum indicates an increase in the inertia of photoconductivity in vacuum. In the preceding work <sup>(8)</sup> it was established that polymer II is a hole semiconductor, and the anomalous fact for a hole semiconductor of the suppression of the diffusion photo-emf by air (oxygen) was noted. The same phenomenon, even more pronounced, also occurred in the investigation of photoconductivity

**Fig. 4.** Decay of the photocurrent in polymer II in an exponential sweep: 1—in air; 2—in vacuum. “Instantaneous” relaxation times for polymer II: 1'—in air, 2'—in vacuum.

polymer II. Admission of air (oxygen) into the vacuum vessel led, in some samples, to a decrease in photoconductivity by an order of magnitude. The quenching of photoconductivity by air (oxygen) in a hole semiconductor requires further study.

The main result of the present work is the discovery of photoconductivity and the investigation of its relaxation in acetylene polymers. The presence of a short-time component of the photoconductivity ( $10^{-5}$ — $10^{-4}$  sec.) indicates that the process undoubtedly has an electronic character. The established hyperbolic law of photocurrent decay points to the bimolecular character of the relaxation of photoconductivity. It should be noted that the short-time kinetics of photoconductivity in the polymers studied is similar to that in some dyes <sup>(14-15)</sup>.

In conclusion I express my gratitude to Academician A. N. Terenin and E. K. Putseiko for their guidance in carrying out this work.

Received  
16 VII 1962

## REFERENCES

1. V. A. Kargin, A. V. Topchiev et al., *Journal of the All-Union Chemical Society named after D. I. Mendeleev*, **5**, 507 (1960).
2. A. A. Berlin, M. I. Cherkashin et al., *High-Molecular Compounds*, **1**, 1817 (1959).

3. A. A. Berlin, L. A. Blumenfeld et al., *High-Molecular Compounds*, **1**, 1361 (1959).
4. Il. L. Kotlyarevskii, L. B. Fisher et al., *High-Molecular Compounds*, **4**, 174 (1962).
5. E. K. Putseiko, *Dokl. AN*, **59**, 471 (1948).
6. I. A. Akimov, E. K. Putseiko, in: *Photoelectric and Optical Phenomena in Semiconductors*, Kiev, 1959, p. 301.
7. A. Terenin, E. Putzeiko, J. Akimov, *J. Chim. Phys.*, **54**, No. 9, 716 (1957).
8. V. S. Mylnikov, A. M. Sladkov et al., *Dokl. AN*, **144**, No. 4, 840 (1962).
9. V. V. Korshak, A. M. Sladkov, Yu. P. Kudryavtsev, *High-Molecular Compounds*, **2**, No. 12, 1824 (1960).
10. V. V. Korshak, V. I. Kasatochkin et al., *Dokl. AN*, **136**, No. 6, 1342 (1961).
11. V. V. Korshak, A. M. Sladkov, Yu. P. Kudryavtsev, *Dokl. AN*, **144**, 115 (1962).
12. N. A. Tolstoi, P. P. Feofilov, *UFN*, **41**, 44 (1950).
13. N. A. Tolstoi, *Izv. AN SSSR, ser. fiz.*, **15**, 712 (1952).
14. E. K. Putseiko, *Dokl. AN*, **132**, No. 6, 1299 (1960).
15. E. K. Putseiko, *Dokl. AN*, **138**, No. 6, 1381 (1961).

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

*Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.*